STUDIES ON THE CORROSION BEHAVIOUR OF MILD-STEEL UNDER SIMULATED INDUSTRIAL CONDITIONS

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By

Ramya Sankar M.S.
(213CH1123)

Under the Supervision of

Dr. Hara Mohan Jena

Department Of Chemical Engineering
National Institute of Technology, Rourkela
Odisha, India
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CERTIFICATE

This is to certify that the thesis entitled "**Studies on the Corrosion Behaviour of Mild-Steel Under Simulated Industrial Conditions"** submitted by **Ramya Sankar M.S. (213CH1123)** at National Institute of Technology, Rourkela is a record of bonafide research work under my supervision and is worthy of consideration for the award of the Degree of Master of Technology in Chemical Engineering of the institute. The candidate has fulfilled all prescribed requirements and the thesis, which is based on candidate's own work, has not been submitted elsewhere for a degree or diploma.

Date:

Place:

Dr. Hara Mohan Jena

Assistant Professor
Department of Chemical Engineering
National Institute of Technology
Rourkela

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213CH1123

ABSTRACT

Corrosion is the deterioration of physical properties of the material due to a reaction with its environment. It converts refined metal to their more stable oxide. Corrosion of the material will depends on mainly on two factors the material of construction and the environment present.

In the present study, an attempt has been made to find the responsible factors in both the aqueous environment and the material of construction. Characterization of the water used for the quenching purpose in Rourkela Steel Plant, Odisha yielded the list of contaminants present in it. The effect of the presence of these compounds on the rate of corrosion has been studied by performing experiments using simulated quenching processing water which is later affirmed by the literature available. The reference level used for the study is taken from the reported literature values as well as from the obtained experimental results. The single effects as well as the combined effects of the water quality parameters are also taken to account for the corrosion study. An inhibitor is used to check the inhibiting efficiency of the selected chemical.

The surface morphology has been studied by SEM and XRD analysis which detects the type of corrosion taking place. EDX analysis of the quenching water establishes the presence of oxygen, carbon and sulphate. XRD analysis infers the formation of various corrosion products such as FeO, $Fe_2O_3$and Fe_3O_4 etc. Literature suggests parameters such as hardness, BOD, COD and presence of various elements such as chloride, sulphate, nitrite, etc. also affects the corrosion rate of a material. On characterisation of the quenching water, the following parameters were obtained: BOD 110.56, DO 10.00, COD 508.80, Hardness 400.96, phenol 70.08, sulphate 7.68, Chloride 223.00, Nitrite 0.20, Ammonia 116.80, and finally organic nitrogen as 246.60 mg/l. Another important parameter which plays a role in the rate of corrosion is the formation of passive layer on the surface of the metal. A wide range of chemical compounds are known to inhibit corrosion in various environments. In the present work, aniline was studied to determine its corrosion inhibition efficiency. The results show that aniline was highly efficient against corrosion due to chlorides while least efficient against corrosion owing to phenols. Aniline was found to be suitable for low-temperature range and lost its knack as the temperature was increased. Thus the problem of corrosion can be under took by utilizing the information obtained from the present investigation.

Keywords: Mild steel, Corrosion, Quenching water, Steel Plant, Aniline, Inhibitors.

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1. INTRODUCTION AND LITERATURE REVIEW

1.1. MILD STEEL

Among various grades of steel, mild steel is widely used and one of the cheapest types of steel available. It has its uses in almost every metal application. Mild steel contains less than 2 % carbon, which makes it respond efficiently to magnetization. Since it is relatively cheaper, mild steel is advisable for major projects requiring vast amounts of steel. Mild steel relatively lacks the property of structural strength, making it undesirable for building girders or structural beams.

Mild steel is a variation of hard steels, which makes it considerably less brittle and increases its flexibility. Among all the products made from steel, some amount of mild steel is present in each of them. Its high ductility nature makes it easy to weld. In the same place, high-carbon steels, such as stainless steel, requires the use of specialized welding methods and techniques. Also, electricity flows through mild steel easily without affecting its structural integrity.

1.2. PROPERTIES AND USES

The properties and uses of mild steel in various fields of technology are the followings (Uzorh.,2013)

• The average density of industry grade mild steel and the young's modulus are 7861.093 kg/m3 and 210,000 MPa

• Addition of carbon changes the properties in steel. Carbon atoms occupies the interstitial sites within the iron lattice, making it stronger and harder. However, the hardness comes at the cost of a reduction in ductility.

• Compared to other different grades of steel available in the market, this type is ideal for welding purposes, as it conducts electric current efficiently without affecting the metal surface.

• Mild steel has ferromagnetic properties, which make it suitable for the manufacture of electrical devices and motors. It yields itself readily to magnetization.

• Mild steel is the best choice for use in the construction of pipelines, building materials and many other daily-use essentials because of their hard, brittle and malleable properties.

• Mild steel can be machined and formed efficiently because of its intrinsic adaptability. It can be solidified with carburizing, making it the perfect material for delivering a scope of shoppe items.

• The high measure of carbon likewise makes it defenceless against rust. Characteristically, individuals incline toward stainless over mild steel when they need a rust-free innovation. It considered as a part of building the foundation and structural steel, other than these, widely used in the auto manufacturing industry.

The chemical composition of the mild steel has been enlisted in Table 1.1.

Table 1.1: General Composition of Mild Steel

Element	Content
Carbon (C)	0.14 - 0.20 %
Iron (Fe)	98.81 - 99.26 % (as remainder)
Manganese (Mn)	0.60 - 0.90 %
Phosphorous (P)	≤ 0.04 %
Sulphur (S)	≤ 0.05 %

1.3. CORROSION

Corrosion of metal is the destruction or material loss that has been explained by the electrochemical reactions took place mild steel surface, and it is not possible without the presence of an electrolyte. It is basically removal of iron atoms from steel and their dissolution in the surrounding environment as Fe^{2+} ions. Corrosion is a characteristic property of a material that does happen by their series of chemical reactions such as oxidation-reduction in order to come back to their original metal state. It is one of the leading causes of pipeline leakages and breaks. The leakages caused as the result of the exposure of the surface of the pipeline to the eroding environment.

Steel is a material of common use in industries due to its low cost and high mechanical strength. However it suffers the severe attack in service, particularly in oil and gas production systems. Although corrosion inhibitors are the most efficient and adaptable way for the in industrial systems the selection and application of inhibitors are actually little difficult because of variable corrosive environment in these systems Corrosion is occurred widely through all distinct types of pipeline. Mitigation of corrosion in onshore transmission

pipelines is accomplished by the combination of the cathodic protection (CP) and dielectric coating systems.

Corrosion can be divided into distinct groups based on the similarities and dissimilarities exhibited in the process. However, many of these forms are not displays the unique mechanism but they shave the overlapping characteristics of different mechanisms. These may be responsible for the initiation or propagation of a particular type of corrosion. The most familiar and often used categorizations based on their morphological characteristics are of eight forms. They include uniform attack, crevice corrosion, pitting, intergranular corrosion, selective leaching, erosion corrosion, stress corrosion, and hydrogen damage. Other main types of corrosions which is avoided by classification group (for example, pitting and crevice corrosion) as they relate particular metals and alloy Substantial advances in the field of corrosion science have begun to define the mechanism of many forms of corrosion more precisely. However, rather than placing the tools into distinct categories, to overlap between many of the forms has become greater. Since there is evidence that hydrogen may dominate the crack initiation or propagation portion of fracture in some metal surface where stress corrosion cracking occurs.

Corrosion can be classified in various ways, such as

- Chemical and electrochemical
- High temperature and low temperature
- Wet corrosion and dry corrosion.

1.4. CORROSION MECHANISM

The corrosion is defined as the removal of iron atoms (Fe) from steel and their dissolution in the surrounding solution, appearing as ferrous ions (Fe^{2+}) The dissolution of steel causes the loss of material, and the cross section becomes smaller. As the result of corrosion the rust is formed, for this process to occur, moisture and oxygen must be present, and both of them are available for the reaction with the metal. However, due to the high alkalinity of surrounding environment (pH > 13), steel will be able to form a very thin film (~ 10 nm (0.01 μm)) called the passivation layer ,which acts as a protective coating that prevents the metal from taking part in the corrosion process. Unfortunately, this layer can be disrupted due to either carbonation or chloride ion attack. The chemical reactions are similar for both of them (Islam and Chowdhury, 2003).

The detailed process of corrosion involves two separate electrochemical reactions in a coupled manner take places at the two different sites of the steel surface simultaneously. These simultaneous chemical reactions are commonly known as anodic and cathodic reactions. The areas on which the chemical reactions occurs are generally known as cathodic and anodic areas. The anodic and cathodic chemical reactions can be explained as below.

Anodic reaction

$Fe \rightarrow Fe^{2+} + 2e^-$ **(**1.1)

Metallic atoms ions dissolved → at the steel surface in the solution

Cathodic reaction

$½\ O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$ (1.2)

Dissolved oxygen Dissolved ions → molecules in the solution

$Fe^{2+} + 2OH^- \rightarrow Fe\ (OH)_2$ (1.3)

Ferrous hydroxide

$4Fe\ (OH)_2 + O_2 + 2H_2O \rightarrow 4Fe\ (OH)_3$ (1.4)

Ferric hydroxide

$2Fe\ (OH)_3 \rightarrow Fe_2O_3.H_2O + 2H_2O$ (1.5)

Hydrated ferric oxide (rust)

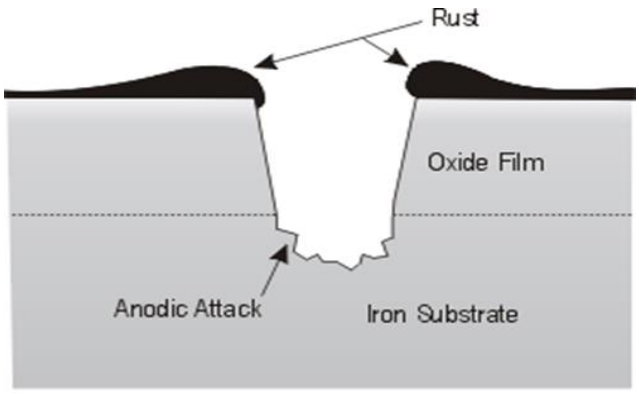

Figure 12.1: Corrosion Mechanism

Figure 1.1 shows the Corrosion Mechanism. The hydrated ferric oxide has a volume of three to six times that of the original volume of Steel (Broomfield, 1997). Internal corrosion is a real reason for pipeline deteriorations and can approach 50% of all occurrences. Pipeline failure is mostly because of setting an area of limited corrosion. Real pipeline failures rates rely on upon the setting rate and the wall thickness.

1.5. DIFFERENT TYPES OF CORROSION

1.5.1. General Attack Corrosion

General Attack corrosion is also called as uniform corrosion. It is the most common type of corrosion seen in day to day life. This type of corrosion results in the deterioration of the whole metal or alloy due to the chemical reaction take places on the exposed surface .As the result of this corrosion the decay of the material and thus leads to the metal failure. Uniform corrosion accounts for the greatest amount of material loss, but this is the safest type of corrosion because we can predict the loss, and it can be manageable and controllable.

1.5.2. Localized Corrosion

Localized corrosion is entirely different from the uniform corrosion; it concentrates on the localized sites. It can be classified in to three different types explained below:

• **Pitting corrosion**: It comes under the class of localized corrosion. By which this corrosion the holes and pits are formed. It is considered to be the most dangerous types of corrosion. It is a type of corrosion the attack is concentrated to smaller areas. It starts from the formation of micro pits and the formed corrosion products will get deposited on the surface and it can be leads to the failure of the all engineering system. The formation of micro pits initiated in the presence of oxygen and the chloride ions accelerated the corrosion. The corrosion can be explained by the factor pitting factor (ratio of deepest pit to average penetration)

• **Crevice corrosion:** It is also similar to the pitting corrosion, take places in a confined space called crevice. This type of corrosion mainly seen in contact areas between the parts, under the seal and gaskets, spaces filled with deposits etc. The conditions leads to the formation of crevices are the depletion of oxygen or the presence of acidic conditions.

• **Filiform corrosion:** It is another main subdivision of localized corrosion generally connected with the aluminium and magnesium alloys. This type of corrosion mainly seen where the conditions are slightly above room temperature and relative humidity is of about 75%.Normally due to this type of corrosion the material loss is considerably very less.

1.5.3. Galvanic Corrosion

Galvanic corrosion is also known as dissimilar metal corrosion. When galvanic couple forms one of the metals becomes cathode and other becomes anode. For galvanic corrosion to occur it should satisfy three conditions they includes:

- The metals should be electrochemically dissimilar

- There should be an electrical contact
- An electrolyte environment should be present.

1.5.4. Environmental Cracking

Environmental cracking can be explained as brittle fracture of a typical ductile material caused by the environmental factors. There are four different types of environmental corrosions are present due to the combined effect of chemicals, temperature along with stress-related conditions.

• Stress Corrosion Cracking
• Corrosion fatigue
• Hydrogen induced Cracking
• Liquid metal embrittlement

1.5.5. Flow-Assisted Corrosion (FAC)

The corrosion takes places due to the passage of high-velocity air or fluid accelerates the elimination of the protective passive layer formed on the metal surface. This causes the explosion of an underlying metal surface to corrode and further deteriorate. This type of corrosion is commonly known as Flow-assisted or flow accelerated corrosion.

• Erosion – assisted corrosion
• Impingement
• Cavitation

1.5.6. Inter - granular corrosion

Intergranular corrosion is also known as intergranular attack. The attack is usually related with the deposition of particular elements or the formation of a compound in the boundary. The corrosion gives preference to attack on the grain boundaries the entire material loss can happens in the severe case of inter granular corrosion. The main reason for the intergranular corrosion is due the presence of intrinsic impurities.

1.5.7. De-Alloying

De-alloying or selective leaching is the corrosion of a specific element in the alloy which includes dezincification of unstabilized brass. The dezincification is used to prevent deterioration and porous formation in copper metal.

1.5.8. Fretting corrosion

Fretting corrosion occurs due to the repeated wearing or vibration on rough surface. As a result of fretting corrosion the pits and grooves are formed on the surface. It is commonly found in rotation and impact machinery, bolted assemblies and bearings.

1.5.9. High-Temperature Corrosion

The compound that can produce low- melting point compounds with a low melting point will mainly produce High-temperature corrosion. The compounds are highly corrosive to metal alloys resistant to high temperatures and corrosion, including stainless steel. High-temperature corrosion can also be caused by high-temperature oxidization, sulfidation, and carbonization.

1.6. CORROSION ON THE MILD STEEL

Iron and steel pipes are used in water distribution systems from almost over five centuries. When the iron is brought in contact with the atmospheric and surrounding aqueous conditions they reaches to the state of Fe(III) as to acquire the thermodynamic stability In water distribution the corrosion products will get deposited in the pipes, these scales not only restricts the flow but also degrade the quality of water (Snoeyink et al.2011,). A lot of research work is going on to quantify the effect of water parameters on the corrosion of iron pipes (Eliassen et al., 1956)

There are numerous water parameters that affect the deposition of scales, erosion of pipes in water distribution systems. The Table 1-2 includes the different corrosion products formed(Cornell and Schwertmann., 1996).Depending on the environment in contact with the pipe surface, the formed corrosion products are relatively soluble Fe (II) solids such as ferrous hydroxide. Scales are produced layer by layer. Under the layer of scales, iron in the form of Fe (II) oxides may be present.

Table 1.2: Different corrosion products formed by atmospheric conditions (Chang T and Lansing F Atmospheric Corrosion of Mild Steel, 2011)

Oxides		**Hydroxides**		**Others**	
Hematite	β -Fe_2O_3, α-Fe_2O_3	Ferrous hydroxide	$Fe(OH)_3$	Ferrous chloride	$FeCl_2$
Maghemite	Fe_3O_4	Goethite	α-FeOOH	Ferric chloride	$FeCl_3$
Magnetite	Fe_5HO_8	Akaganeite	β-FeOOH	Ferrous sulphate	$FeSO_4$
Ferrihydrite	Fe_4H_2O	lepidocrocite	γ-FeOOH	Ferric sulphate	$Fe_2(SO_4)_3$
		Feroxyhyte	δ-FeOOH		

1.7 QUENCHING PLANT CORROSION

The iron and steel sector is the second-largest industrial user of energy. Coke quenching performs as the most effective system to reduce air pollution and at the same time a remarkable energy efficient process also. The quenched coke will be harder and stronger, and its moisture content is much lower than that of the untreated quenched coke. The major steps involved in the production of finished steel includes coke production, sinter production, iron and steel making, casting of iron finally shaping and finishing. In coke ovens naturally found coal is converted into coke, which is suitable for the use in metallurgical industries in blast furnace, in foundry and for domestic purpose. Large quantity of water is used for the purpose of quenching of hot coke and also for washing gas produced from oven. Water used for quenching the coke discharge from the retorts or oven, it contains hazardous components that are difficult to handle. They include suspended matter of coke breeze, ammonia, phenol, cyanides, and nitrites. These are highly and toxic and responsible for severe corrosion.

Many of the pollutants in the process water are the result of compounds found in the charges and fluxes added to furnace. In batch iron and manganese blast furnace operations ammonia present in the exit gas as the result is present in the waste water. The ammonia is formed from the coke charge during the blast furnace operations. Manganese is present in waste water from ferromanganese production and other elements may be present depending on the various ores and alloys used in production. Lastly cyanide is generated as a result of the reaction of nitrogen in the blast furnace air with carbon from the coke charge in the reducing atmosphere of blast furnace.

The water required in various processes in the steel plant may be used once and reused or recycled. In the reuse system, the water used in one process unit is used again in the other production process with suitable treatments. The effluents from coke oven and the by-products of plants are treated by biochemical oxidation of cyanides, ammonia and phenol. The treated effluent from BOD plant may be reused in the quenching hot coke ovens. In recent years due to the use of these treated water the corrosion was increased to a very high level and it lead to be an economic problem. For these reasons research interest in this field has increased many fold.

Several water quality parameters can influence the formation of corrosion scales in the iron or steel pipes in water distribution systems. Whereas the corrosion rate is measured by weight loss from the metallic iron release and the water quality analysis. This gives an idea for

conducting the research and gives an appropriate efficient and economical method for the treatment of the corrosion environment.

Various parameters that affects the rate of corrosions are:

- Temperature and pH
- Flow velocity
- Dissolved gas
- Sulphur effects
- Phenol effects
- Nitrogen compounds
- Cyanides

1.8.EFFECT OF DIFFERENT PARAMETERS ON CORROSION

1.8.1. Effect of Temperature and pH

Two distinct mechanisms of carbon dioxide corrosion were recognised from research and technology development, i.e., low temperature (<60^{o}C) and high temperature (60- 150^{o}C). At low-temperature, CO_2 corrosion is a function of pH, salt concentration, temperature, $CO_2$and metallurgy of the low alloy steel. However, at high temperature, CO_2 corrosion is influenced by system hydrodynamics because of a change in the surface electrochemistry a number of authors have found that the temperature strongly affects the conditions needed to form protective iron carbonate layers. At lower temperatures (<60^{o}C) the solubility of $Fe_2 CO_3$ is high and the precipitation rate is slow, and protective films either will not form or may still build up but are not protective due to their open porous structure and reduced bond with the substrate metal (Popova,2007).This may have been influenced by the experimental conditions under which the films were formed unless the pH is increased. In this temperature range, the corrosion rate increases with temperatures up to an intermediate range of 60-80°C.In any case; the impact of temperature on corrosion can be more confused. A high water temperature decreases the solvency of calcium carbonate in water, which advances scale development and moderates corrosion. Temperature additionally adjusts the manifestation of corrosion. Pits and tubercles have a tendency to frame in chilly water while high-temperature water advances uniform corrosion (Robert and Boris, 2010). Uniform corrosion spreading over the whole surface of a pipe is far less tricky than tuberculation, so high temperatures can appear to moderate the destructive procedure. An increment in the temperature causes a reduction in the stress corrosion life. As the pH getting increases the solution becoming more corrosive.

The ions are free to move in the high pH solutions and they reacts with the sample present and thus the corrosion becomes severe.

1.8.2. Effect of flow velocity

The impact of flow velocity on corrosion is additionally rather complex. Moderate flow rates are the most suitable since they advance the development of scale without loosening up tubercles. At low flow speeds, corrosion is expanded and has a tendency to be as tuberculation because of the presence of oxygen concentration cell corrosion. At high flow rates, abrasion of the water against the pipe has a tendency to wear the pipe away in an altogether different manifestation of corrosion. High flow speeds likewise evacuate inhibiting scale and tubercles and enhances the contact of the pipe internals with oxygen, all of which will expand the rate of corrosion. The effect of flow velocity can be correlated with both of the physical and chemical characteristics of the corrosion product layer (Seheers, 1992).

1.8.3. Effect of Dissolved gases

The corrosion rate observed in the environments with oxygen is higher as compared to without oxygen. During the electrochemical reaction oxygen acts as a cathodic depolarizer, thus removes hydrogen from the cathode then allows the corrosion attack to continue. The effect of oxygen on corrosion with metal in a closed vessel increases with temperature.

Dissolved oxygen (DO) acts as an electron acceptor in the corrosion of metallic iron. Dissolved oxygen will also plays a role in the oxidation of iron

$$Fe\ (metal) + 0.5O_2 + H_2O \leftrightarrow Fe^{2+} + 2OH^- \quad (1.9)$$

$$Fe^{2+} + 0.25O_2 + 0.5H_2O + 2OH^- \leftrightarrow Fe\ (OH)_{3(s)} \quad (1.10)$$

$$3FeCO_3\ (s) + 0.5O_2 \leftrightarrow Fe_3O_4\ (s) + 3CO_2 \quad (1.11)$$

$$4Fe_3O_{4\ (s)} + O_2 \leftrightarrow 6Fe_2O_{3(s)} \quad (1.12)$$

Thus, the concentration of oxygen will shows a varying effect on iron corrosion. Generally the corrosion rate increases with increases with the dissolved oxygen content. The lower dissolved oxygen content will not show any tuberculation, but it shows a higher turbidity. The formation of protective oxide film on the metal surface by the reaction with the metal composition will decide the corrosion resistance of the carbon steel (Ismail and Adan, 2014).The instability of passive film facilitates the delivery of oxygen towards the metal surface and promotes the oxygen reduction that accelerates the corrosion rate. The oxygen diffusion normally determines the rate limiting step of corrosion rate through the passive film

(Kim et al., 1997).The ability of buffer ions including phosphates can show a corrosion inhibition property their DO content can vary the inhibition property.

1.8.4. Effect of presence of Sulphur compounds

Due to its low cost, high mechanical strength and excellent corrosion resistant the mild steel is widely used in the industries as building blocks. Sulphide pollution of seawater is usually occurs as result of discharge of industrial waste water, and the biological and bacteriological processes which enhances the corrosion rate of steel (Hamdy et al., 2008). In the presence of suspended particles the chloride and sulphide has a marked effect on the corrosion protection and performance of the mild steel.

Sulphur is one of the leading corrodent that causes difficulties in the refinery industry. The presence sulphide in the environment causes the performance of mild steel in response it will cause the economic and human loss (Hucińska, 2006).

Erosion-corrosion occurs when a metal is exposed to the flowing corrosive environment. Passivity caused by film formation is absent in this case. As soon as the film is formed it is eroded by the flowing environment, bringing the new surface of the metal in contact with the corrosive environment. Although the summarized effect of erosion and corrosion is very dangerous, the complete mechanism is still on under investigation (Hamdy et al., 2008).

Both iron and sulphur species are susceptible to oxidation and sulphur produces more quickly more oxides to sulphates and sulphites that can increase the acidity of the flowing fluid. Elemental sulphur can readily form in aqueous systems via the oxidation of sulphide species (Fang et al., 2008). Possible reactions for the formation of elemental sulphur (S_8) could involve high oxidation state metal (denoted Mn+) or oxygen:

$$8\ H_2S_{(aq)} + 16\ Mn^{+}_{(aq)} \rightarrow S8_{(s)} + 16\ H^{+}_{(aq)} + 16\ M\ (n-1)^{+}_{(aq)} \qquad (1.13)$$

$$8H_2S_{(aq)} + 4O_2\ (g) \rightarrow S8_{(s)} + 8H_2O_{(l)} \qquad (1.14)$$

Also to strictly chemical processes, sulphide oxidizing bacteria have been shown to form liquid sulphur droplets under ambient conditions; consequently, the formation of elemental sulphur is almost inevitable in H_2S corrosion environments in the field. Elemental sulphur is shown as S8 in the reaction equations below as that represents the stable allotrope of sulphur under standard conditions (Sheraret al., 2013). Acidification in sulphur containing aqueous systems has been reported, with species such as H_2S, H_2SO_2, H_2SO_3, H_2SO_4 and polysulfide

being possible candidates as hydrolysis products. Acid formation as a result of sulphur hydrolysis was the primary factor governing corrosion in the presence of elemental sulphur.

$$S8_{(s)} + 8\ H_2O_{(l)} \rightarrow 6\ H_2S_{(aq)} + 2\ H_2SO_{4\ (aq)} \quad (1.15)$$

Alternatively, (MacDonald et al., 1978) hypothesized an electrochemical reaction between iron and polysulfide is the driving force for corrosion in systems where elemental sulphur is present.

The main damage caused due to the presence of sulphur are the weight loss and the stress cracking. The low-temperature environment includes the aqueous environment, and high temperature includes the non-aqueous environment (White etal.1986).The activity of carbon toward steel increases with the increase in the sulphur quantity and simultaneously the stability of carbides decreases. The carbon that released from carbides diffuses into the steel thus the rate of corrosion increases. The hydrogen content supports the process of carbide destabilisation (Hucińska et al., 2006).

1.8.5. Effect of presence of Phenol

The most commonly seen pollutant in the industrial waste water is phenol and phenolic compounds. In the oil refineries, petrochemical, ceramic and in steel plants and in coal conversion process a very high amount of phenol and phenolic compounds are present (Taghavi et al., 2012). In steel plants, it is generated in coking facility plants. For the removal of phenol we can use the burning process it is not at all a ecological problem but it will cause an economic problem because of the presence of very huge amount of water. A typical concentration of phenol in the effluent water is 6.8 wt. %.

By the small addition water in the range of 0.2% to 0.6% to anhydrous phenol is found to decrease the corrosion rate, the corrosion rate of low-carbon steel markedly, although huge amount water can increase the corrosion rate. At the same time small amount water enhances the formation of blue-black film on the surface, thus the corrosion rate is getting decreased.

The refining processes currently used in the industry involves high amount of phenol at high temperatures. So many investigations have been conducted by simple experimental procedure to find out the critical factors which determines the corrosion rate. A comparison between pure phenol and sulphur containing phenol the second one shows more corrosion. Phenol containing sulphur compounds was more corrosive in general to various metals than pure phenol (Sirajuddin et.al.,2008)

1.8.6. Effect of Presence of nitrogen compounds

The main three oxidation reduction reactions include nitrification, denitrification and nitrate reduction to ammonium nitrites are the common intermediate. In the case of mild steel present in nitrogen containing environment they are supposed to undergo the above reactions. Depending on the reaction conditions the toxic nitrites get deposited on the surface leads to an increase in the corrosion rate. The results strongly support the view that intergranular stress corrosion cracking of mild steel in nitrate solutions is related to passivation phenomena. Under certain conditions, the grains may already be passivized while grain boundaries are still active (Baba et al., 2002).

If no other impurities are present in the surroundings oxygen will forms a thin film on the surface of steel coupon which inhibits the further corrosion to some extends depending on the concentration and the strain rate. The nitrogen or ammonia present in the environment inhibits the formation of this film on the bare surface, a competitive adsorption will take place and thus the nitrogen compound will have an additional effect on the formation of passive film (Karim and Mustafa.,2010).

1.8.7. Effect of Presence of chlorine compounds

Chlorine is as very strong oxidizing agent for all metallic and organic species present. The reaction of chlorine with iron is shown below:

$$HOCI + 2Fe^{+} + 5H_2O \rightarrow 2Fe(OH)_3\downarrow + Cl^{-} + 5H^{+} \quad (1.16)$$

The main chlorine corrosive environments are created by NaOCI solution, as calcium hypochlorite granules, and as chlorine dioxide ($C1O_2$).The corrosion resistance on the metal lies on the capacity of the surroundings to form an inhibiting layer on the surface. The formed layer will cover all over the surface which fill opposes the continued oxidation or rusting (Andijani and Mobin,2005). The formation of this layer is an instantaneous process in oxidation of air or with different fluids contains oxygen. When the layer is formed we can say that the metal has got passivized there will be a considerable reduction of the corrosion. In the case of chloride, they are highly active they will quickly penetrate the corrosion attack to occur.

As the passivated layer breaks, further corrosion will takes places. In the case of chloride the accelerated corrosion is greater in some areas than the others. The passivated layer formed on the surface gets breaks on the few areas and the chloride ions gets penetrated to the surface the pitting corrosion starts. This difference in relative regions quickens the corrosion, creating

the pits to enter deeper. The electrolyte fills the pits and keeps the oxygen from passivating the active metal, so the issue deteriorates. This sort of corrosion is frequently called concentrated cell corrosion (Arthur and Richard, 1998).

At this state the metal piece will be under the tensile stress condition the pits formation process becomes more fast. There is the possibility of formation cracks also on the surface due to the effect of tensile stress. Ordinarily, there will be more than one split present bringing about the sample to look like a cobweb's. Chloride stress cracking is a difficult issue in the industry and not frequently perceived by the individuals, mainly by the combined effect of sulphides also (Padilla and Alfantazia, 2014). Some extra information about chloride stress breaking that we need to know:

•The commonly used series in industry are 300 series grade steel due to its high mechanical and good corrosion resistant properties. But the chloride corrosion towards this type steels is very severe.

•The most types of insulating materials available are contains chlorides. The pipes undergo stress corrosion as the piping is frequently under goes tensile stress (Rafaey et al.,2013).

1.8.8. Effect of Presence of cyanide

Cyanide is a most corrosive and toxic element ever seen. It is a triple bonded molecule showing different oxidation states of +2 and -3. The cyanides present in the environment are mainly due to the metal finishing and mining industries. Cyanides occur in water as hydrocyanic acid (HCN), cyanide ions(CN^-)simple cyanides and metallic cyanides and a single chain complex ring compound.

The behaviour of mild steel in aqueous cyanide solutions similar to caustic cyanide elution solutions was investigated at high temperature in electrochemical experiments. The anodic polarization diagrams of mild steel indicated that steel may undergo active dissolution under these conditions. The presence of cyanide will favour the dissolution of iron to form a ferrous cyanide complex Cyanide in aqueous solution may change the behaviour of iron by the formation of soluble iron cyanide complexes in preference to insoluble oxides.

At higher concentrations of either hydroxide or cyanide gave rise to an increase in the active peak current densities. Cyanide additions caused the active potential region to expand and increased the peak current densities significantly. This effect was more pronounced at higher hydroxide concentrations but increased current densities were also noted at lower pH values. At pH less than 11 cyanide ions combines with hydrogen. At pH greater than 12, CN^- ions are

available in the free form. In the presence of other general effluent components like ammonia, hydrogen sulphide and carbon dioxide, cyanide ions because increased corrosion rates in carbon steels. Cyanide concentrations in the range of 20 to 100 ppm are present in industrial wastes. Corrosion rate increases with increase in temperature and cyanide content (De wet and sundenbergh, 1993).

The important preliminary step to find out the appropriate solution to the corrosion problem is the determination of various symptoms and the mechanism of the processes. Here explains the main five approaches towards the control of corrosion:

- Change the material of construction to a more appropriate material
- By the use of inhibitors modify the corrosion environment.
- By providing suitable coatings to the surface (metallic or organic)
- Design modifications to the system or component.

The design modifications includes provide adequate ventilation and drainage to minimize the accumulation of condensation. By avoiding the depressed areas where drainage is not proper. Avoid the use of absorptive materials such as asbestos, fabrics etc. which are in contact with the metal surface. Provide easy access for the purpose of corrosion.

1.9. SCALE ANALYSIS

Corrosion induces material loss and further leads to the failure of certain parts or machineries which causes serious troubles in the industries. The major problems that occurs due to corrosion includes the increase repairing cost, loss of the useful contaminated products (precipitates formed),the economic and environmental damage can affect to even human also. The natural consequence of their temporary existence in metallic form plays the driving force for the corrosion. The primary corrosion product of iron exists as, e.g. $Fe(OH_2)$, or more likely $FeO{\bullet}nH_2O$, but the action of oxygen and water can yield other products having different colours(Kairi and Jain,2013).

- $Fe_2O_3{\bullet}H_2O$ (hydrous ferrous hydroxide) represented as Fe (OH) $_3$, is the principle component of red-brown rust.
- $Fe_3O_4{\bullet}H_2O$ (hydrated magnetite) sometimes called as ferrous ferrite, represented as ($Fe_2O_3{\bullet}FeO$), most often green but can be deep blue in the presence of organic complexants.
- Fe_3O_4 or magnetite normally present in the colour of black.

Basically scaling can be explained as the deposition of minerals or the products formed due to the electrochemical reactions take place in the metal surface or the waterlines of the containers. Commonly we call it as rusting. In general scales precipitated on the metal surfaces provide protection to the surfaces from the other severe types of corrosion. In other point of view scales are defective, they forms cracks and pits on the surface. The type of formed scale determines the corrosion and the corrosion rate.

1.10. CORROSION INHIBITION

The corrosion makes severe economic losses to the plants due to the different effects of environment. These can be reduced by the application of certain chemical compounds, they are commonly known as inhibitors. Erosion and scaling of carbon steel may be restrained by the utilization of inhibitors. Most widely used methods for the corrosion inhibition is the chemical treatment methods. It includes the use of inhibitors. The corrosion inhibitors are commonly selected depending on their properties. They are promising, effective, and flexible and cost attractive method to reduce the corrosive attack of acid solutions. Corrosion inhibitors are chemical compound usually used in small concentration which when added to a corrosive media retards the corrosion process and keeps its rate to a minimum. It has been watched that the impact of corrosion inhibitors is constantly brought about by a change in the condition of the protected surface because of assimilation or development of barely dissolvable mixes with metal cations. A survey including broad listing of different sorts of natural inhibitors has been published (Mohammad et al., 2014). The frequently utilized corrosion inhibitors are nitrogen, sulphur, oxygen and phosphorous containing mixes. These mixes get adsorbed on the metal from the bulk of the environment and construct a film on the metal surface. The Inhibition Efficiency (IE) increments in the pattern: O<N<S<P. The erosion inhibition of metals in acidic media by different of natural mixes has been broadly studied. The inhibition activity of natural atoms is because of their adsorption on the surface of the metal through the presence of activity centres. Rhodea et al.(2013)have assessed the impact of phenol on the erosion of mild steel in nitric acid of different concentration. The percent loss in weight was found to increment straight with an increase in acid concentration.

The important parameters need to be taken into account when assessing corrosion inhibitors, such as:

- Effectiveness of the compound
- The activity of the compounds towards the products covering the metallic core
- The effects of new compound in the corrosion effects

1.11. SCOPE OF PROJECT

It is a well-known fact that industrial effluents are the major cause of corrosion and it contains more than one component in it with concentration continuously varying due to large scale operations. Literature review suggests that a reasonable amount of work has been done in this field. Although it is an interesting topic from last two centuries, most of the notable work is confined to a particular environment. There has been very little work reported constituting multiple corrosive agents. To develop a corrosion inhibition mechanism for an industry, it should be necessary to understand the corrosion at large scale. The understanding can be used to develop an inhibition technology and corrosion predictive modelling. Predictive modelling can help in determination of life span of machinery used in corrosive environment. So far researchers have studied a large number of corrosive environments but no any significant work has been done to collect and standardize these data. Further quantification of material loss by corrosion at different concentrations of various chemicals present in the industrial effluent is necessary. For a few years Rourkela steel plant is facing a major problem of material loss due to corrosion of the quenching equipments. Corrosion became severe when the BOD treated water is used instead of the technical water earlier used in quenching. Thus, there is a scope to study the corrosion behaviour of quenching equipment under the environmental and operating conditions, as they are in the quenching plant.

To study the corrosion behaviour of the materials of the quenching plant, the steps could be identification of types of corrosion taking place to the quenching equipments, characterising the environmental and water used in quenching, study the material loss because of corrosion under simulated conditions and study the role of inhibitors in inhibiting the corrosion.

1.12. OBJECTIVE OF THE PROJECT

The major objectives of the current investigation are the followings:

- Study of surface morphology to identification of the type of corrosion taking place to the quenching equipments present in the steel plant.
- Determination of the responsible factors for the corrosion, which is present in the water used in the quenching plants.
- Determination of the material loss under the simulated quenching unit processing water of individual and combination of different chemicals at specified concentrations and at specified temperature conditions.
- Determination of corrosion inhibition efficiency of a particular inhibitor.

1.15 THESIS OUTLINE

This thesis consists of four chapters:

Chapter 1, presents an introduction and literature review of the process and effects of environments on mild steel corrosion, objectives, scope of the thesis.

Chapter 2, provides materials and methods that are used in this study to characterize the corrosion of mild steel samples, and an overview on inhibition of the corrosion.

Chapter 3, describes the test study and a detailed discussion of the results obtained from the experimental study. And a detailed comparison with investigated results and which obtained from the literature review.

Chapter 4, presents the overall conclusion and future work based on outcomes of present study.

2. MATERIALS AND METHODS

2.8. WASTEWATER COLLECTION AND PRESERVATION

Effluent samples were collected from the quenching pit of Rourkela Steel Plant, Odisha. Water sample was collected in a plastic bottle and stored at temperature below 4˚C. Wastewater was divided into three parts and preserved with different reagents as per the demand of the experiments to be performed. Samples were stored at pH <2, Temp-4˚C (Using HNO_3 or H_2SO_4), pH>10, Temp- 4˚C (Using NaOH). EPA guidelines were used for determination of composition of wastewater.

The samples were analysed as per standard methods for the examination of water and waste water. The methods used for the analysis of the water quality parameters discussed below are used the protocols available on the Environmental protection agency (Standard methods for the examination of water and waste water 14^{th} edition, 1975)

2.9. BIOLOGICAL OXYGEN DEMAND

2.2.1 Required Reagents and their preparations

- Manganous Sulphate solution: 364g $MnSO_4$has been dissolved in one litre of distilled water.
- Alkaline Iodide Sodium Azide Solution: 700 g of KOH and add 150 g of KI were dissolved it in distilled water, and made up to 1000 ml. 10 g of NaN_3has been dissolved in 40 ml of distilled water. These two solutions were mixed thoroughly.
- Sodium Thiosulphate stock solution: 25 g of $Na_2S_2O_3.5H_2O$were dissolve it in distilled water and made up to 1000 ml. 1 g of sodium hydroxide were added to it for preservation.
- Starch Indicator: 2 g of starch has been dissolved in 100 ml of hot distilled water.0.2 g of salicylic acid were added to it for preservation.
- Sulphuric Acid
- Calcium Chloride solution: 27.5 g of $CaCl_2$were dissolved in distilled water and made up to 100 ml.
- Magnesium Sulphate solution: 22.5 g of $MgSO_4$ were dissolved in distilled water and made up to 100 ml.
- Ferric Chloride solution: 0.15 g $FeCl_3$and dissolve it in distilled water and make up to 100 ml.
- Phosphate buffer solution: 8.5g of KH_2PO_4, 21.75 g of K_2HPO_4, and 33.4 g of $Na_2HPO_4.7H_2O$, were added to the same beaker and dissolved in distilled water. Finally

accurately 1.7 g of NH_4Cl has been added and dissolved thoroughly. And made the solution to 1000 ml. The pH should be 7.2 without any further adjustment.

2.2.2 Testing of Sample

Four 300 ml glass stoppered BOD bottles were used two for the sample and two for the blank, 10 ml sample was diluted to 30 times. Out of four in two bottles blank and sample was preserved respectively in BOD incubator at 20ºC for five days .Other two bottles were used for experimentation as the same above but the analysis was done at the same time.2ml of manganese sulphate, 2 ml of alkali-iodide-azide reagent added by touching the surface only. Allow it to settle for a sufficient time in order to react completely with oxygen. When this flock has settled to the bottom, shake the contents thoroughly,2 ml of concentrated sulphuric acid added, from this 203 ml of the solution is titrated with standard Sodium thiosulphate solution until the yellow colour of liberated Iodine is almost faded out. (Pale yellow colour).Starch solution was used as the indicator; the colour change was the disappearance of the blue colour disappears to colourless. Note down the volume of sodium thiosulphate solution added, which gives the D.O. in mg/L. The experiment were repeated for the concordant values. After five days, the samples from incubator is analysed as per the procedure described above.

2.3 CHEMICAL OXYGEN DEMAND

2.3.1Reagents required

- Potassium Dichromate Reagent - Digestion Solution: 4.913 g of $KMnO_4$, 33.3g $HgSO_4$ and 167 ml of conc.H_2SO_4 were transferred it to the beaker. The contents were dissolved and made to 1000 ml volume.
- Sulphuric Acid Reagent - Catalyst Solution: 5.5 g silver sulphate crystals were dissolved in 500 ml of conc. H_2SO_4 and it was allowed standing for 24 hours.
- Ferrous Ammonium Sulphate solution: 39.2g of $(NH_4)_2 Fe(SO_4)_2$dissolved in 1000 ml distilled water.

2.3.2 Testing of sample

Three COD vials with stopper were taken (two for the sample and one for the blank).2.5 ml sample taken in the two COD vials(in one COD vial blank),1.5 ml of potassium dichromate reagent - digestion solution was added to each of the three COD vials.3.5 ml of sulphuric acid reagent - catalyst solution also added in the same manner. Cap tubes tightly. The COD

Digester was switched on and the temperature was fixed at 150º C and time was set as 2 hours. The sample was titrated against ferrous ammonium sulphate with ferroin as indicator, the colour changed from bluish green to reddish brown the volume of ferrous ammonium sulphate solution added to the sample has been noted down .The same procedure is repeated for the blank as well as the sample.

2.10. **HARDNESS**

2.3.1 Equipment and Reagents

• Buffer solution: 1.179 g disodium EDTA,780 mg $MgSO_4.7H_2O$ were dissolved in 50 ml distilled water.16.9 g NH_4Cl and 143 ml conc.NH_4OH with mixing and these two solutions and made up to 250 ml. The pH was in the range of 10.0± 0.1 at end point of the titration.

• Indicator: Calgamite.

• Standard EDTA titrant: 3.732 g di sodium EDTA were diluted to 1000 ml.

• Ammonium hydroxide, 1 N: 70 ml of conc.NH_4OH were to diluted to 1 liter by using distilled water.

2.3.2 Procedure

The sample should require <15 ml EDTA titrant and titration should be completed within 5 minutes of buffer addition. 25 ml sample were taken in titration vessels, and neutralized with 1 N ammonium hydroxide and diluted to about 50 ml. 1 to 2 ml buffer solution and 1 to 2 drops indicator solution were added. Titrated has been done slowly with continuous stirring with standard EDTA titrant until last reddish tint disappears. Solution shown blue at the end point.

2.11. **DISSOLVED OXYGEN CONTENT**

2.4.1 Reagents required

• Manganous Sulphate Solution: 364g $MnSO_4$has been dissolved in 1 litre of distilled water.

• Alkaline Iodide Sodium Azide Solution: 700 g of KOH and 150 g of KI were dissolve in the distilled water, and made up to 1000 ml.10 g of $NaN_3$was dissolved in 40 ml of distilled water. These two solutions were mixed thoroughly.

• Sodium Thiosulphate stock solution: 25 g of $Na_2S_2O_3.5H_2O$ dissolved in distilled water and make up to 1000 ml.1 g of sodium hydroxide is added for preservation.

• Starch Indicator: 2 g of starch dissolve in 100 ml of hot distilled water. 0.2 g of salicylic acid was added as preservative.

• Sulphuric Acid

2.4.2 Testing of Sample

Two 300-ml glass-stoppered BOD bottle were used and filled it with the sample to be tested. 2ml of manganese sulphate and2 ml of alkali-iodide-azide reagent has been added to the bottle through surface of the liquid. 2 ml of concentrated sulphuric acid added to just above the surface of the sample ,203 ml of the solution taken from the bottle and transfer to a conical flask. Titrate it against sodium thiosulphate using starch as indicator. The end point was the disappearance of the blue colour to colourless. The volume of sodium thiosulphate solution added which gives the dissolved oxygen in the given sample has been noted down. Repeat the titration for concordant values.

2.12. **DETERMINATION OF PHENOL**

2.5.1 Reagents and Equipment

• Spectrophotometer: Wavelength 460 or 510 nm.

• pH meter

• Buffer solution: 16.9 g NH_4Cl in 143 ml conc.NH_4OH and dilute to 250 ml with distilled water. pH were adjusted to a range of 10.

• Aminoantipyrine solution: 2 g of 4AAP were dissolved in distilled water and dilute to 100 ml.

• Potassium ferricyanide solution: 8 g of K_3 Fe $(CN)_6$ were dissolved in distilled water and dilute to 100 ml.

• Stock phenol solution: 1.0 g phenol and diluted to 1 liter.

2.5.2Direct photometric method

To 100 ml of distillate 2 ml of buffer solution is added and mixed. The pH of the sample and standards maintained at 10 ± 0.2. 2.0 ml Aminoantipyrine solution ,2.0 ml potassium ferricyanide solution added and mixed well. After 15 minutes absorbance at 510 nm is noted down.

2.13. **DETERMINATION OF SULPHUR COMPOUNDS**

2.6.1 Reagents and Equipment

• Steam Bath

• Muffle furnace with temperature indicator

• Desiccator

• Methyl Red solution: 100 mg methyl red sodium salt were distilled water in 100 ml.

• Hydrochloric acid 1:1

• Barium chloride solution: 100 g $BaCl_2$dissolved in 1 liter of distilled water

•Silver nitrate-nitric acid reagent: 8.5 g of $AgNO_3$ and 0.5 ml Conc.HNO_3weredissolved in 500 ml distilled water.

2.6.2 Procedure

The pH of the solution was maintained in the range of 4.5 to 5 by using HCl or methyl red solution. The solution was heated to boiling and warm $BaCl_2$ solution is added slowly, until precipitation of the sample was completed; then 5 ml in excess added for the excess precipitation. Digested the precipitate at 80 to 90°C for overnight.

Filtration and Weighing: A little ash less filter paper pulp was mixed with the $BaSO_4$ and filtered at room temperature. The precipitate is washed with small portions of warm distilled water until they got free of chloride .Dried the filter and precipitate. Ignited at 800°C for 1 hour. The precipitate is dried and weighed.

2.14. **NITROGEN, KJEDAHL, TOTAL**

2.7.1 Equipment and Reagents

• Mercuric sulphate solution 8 g HgO is diluted in 50 ml of 1:4 H_2SO_4 and dilute to 100 ml with distilled water.

• Sulphuric acid-mercuric sulphate –potassium sulphate solution: 267 g K_2SO_4 in 1300 ml distilled water, 400 ml conc.H_2SO_4 and 50 ml $HgSO_4$ were mixed together and diluted to 2 litres with distilled water.

• Sodium hydroxide –sodium thiosulphate solution: 500g NaOH and 25 g $Na_2S_2O_3.5H_2O$ mixed together and diluted to 1liter using distilled water.

• Mixed indicator: 2 volumes of 0.2 % methyl red in 95 % ethanol with 1 volume of 0.2% methylene blue in ethanol.

• Boric acid solution:20 g of H_3BO_3diluted to 1 litre with distilled water.

• Sulphuric acid 0.02N

• Ammonium chloride stock solution: 3.819 g NH_4Cl dissolved in distilled water and made up to 1 litre

• Nessler reagent: 100 g mercuric iodide and 70 g potassium iodide were dissolved in a small volume of distilled water.160 g of NaOH in 500 ml of distilled water, the two solutions were mixed together and diluted to 1 litre.

2.7.2 Procedure

Micro Kjeldahl system: 50.0 ml of sample taken in a 100 ml Kjeldahl flask and 10 ml of sulphuric acid –mercuric sulphate –potassium sulphate solution added to it. Heated the mixture until the solution becomes pale yellow this means the SO_3 are given out. Again it boiled for 30 minutes cooled the residue and 30 ml of distilled water is also added. After digestion of the sample 10 ml of sodium hydroxide-thiosulphate solution added without mixing. After the kjeldahl apparatus is connected the condenser tip should be dipped on the boric acid solution. Steam distilled 30 ml at the rate of 6-10 ml/min., into 5ml of 2% boric acid. Dilute the distillate to 50 ml.

2.7.3 Determination Ammonia in the Distillate

Titrimetric determination: 3 drops of the mixed indicator is added to the distillate and titrated with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

Calculations

If the titrimetric procedure is used, calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\boldsymbol{TKN, mg/l} = \frac{(\boldsymbol{A-B})*\boldsymbol{F}*\mathbf{1000}}{\boldsymbol{S}} \qquad (2.1)$$

Where:

A=millilitres of standard 0.020 N H_2SO_4 solution used in titrating sample

B = millilitres of standard 0.020 N H_2SO_4 solution used in titrating blank

N =normality of sulphuric acid solution.

F =milli equivalent weight nitrogen (14 mg).

S =millilitres of sample digested.

If the sulphuric acid is exactly 0.02 N, the formula is shortened to

$$\boldsymbol{TKN\ mg/l} = \frac{(\boldsymbol{A-B})*\boldsymbol{280}}{\boldsymbol{S}} \qquad (2.2)$$

2.15. NITROGEN AND NITRITE

2.8.1 Reagents and Equipment

- Spectrophotometer
- Buffer-colour reagents: 5.0 g $C_6H_8N_2O_2S$ and 0.5 g N-(1-naphthyl) ethylenediaminedihydrochloride. Add 136 g of $CH_3COONa.3H_2O$ dissolved in 105 ml Conc.HCl, and diluted to 500 ml with distilled water.
- Nitrite stock solution: 0.4926 g of dried anhydrous sodium nitrite has been dissolved in distilled water and diluted to 1000 ml. Preserve by the addition of 2 ml chloroform per liter.

2.8.2 Procedure

The pH of the sample were adjusted to the range of 6 with 1:3 HCl. 2ml of buffer-colour reagent is added to each standard and sample, mixed well and waited for the development of colour for at least 15 minutes. The absorbance is noted down at 540 nm for the blank, standard solutions and for sample also. The concentration is found out from the calibration graph plotted for standard solutions.

Calculations

Read the concentrations of NO_2-N directly from the curve.

If less than 50.0 ml of sample is taken, calculate mg/l as follows:

$$\boldsymbol{NO_2\ N, Mg/l} = \frac{\frac{\boldsymbol{mg}}{\boldsymbol{l}}\boldsymbol{from\ std\ curve}*\boldsymbol{50}}{\boldsymbol{ml\ sample\ used}} \qquad (2.3)$$

2.16. DETERMINATION OF CHLORINE

2.9.1 Equipment and Materials required

• Silver nitrate solution: 4.25 g of $AgNO_3$ and dissolve it in 250 ml of distilled water.

• Potassium chromate indicator solution: Dissolve 1 g of K_2CrO_4 in 20 ml distilled water.

2.9.2 Determination of Chloride Ion Concentration by Titration (Mohr's Method)

To 100 ml of 10 times diluted sample 1 ml of chromate indicator were added and it is titrated with 0.1 mole/l silver nitrate solutions. Silver chlorides formed a white precipitate; the colour change of titration is from cloudy solution to faint yellow colour. The titration was repeated for concordant values.

The moles of silver nitrate reacted where found out using the following equation. Use the.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)} \qquad (2.4)$$

2.17. WEIGHT LOSS METHOD

For the corrosion study experiments the most easily simplest and convenient method over all others is weight loss method. For this method we should note down the initial dimensions like length, width and weight, and these dimensions are compared with the samples obtained after the experimentation. The difference in these two will gives the rate of corrosion (Rathi et al., 2010).

2.17.1. Mild Steel Coupon Preparation

Mild steel coupon with the dimension of 2.35cm X 0.95cm X 0.1cm was used as test sample to study the effect of corrosion by weight loss. Sample was obtained as bulk metal from Rourkela Steel Plant, SAIL and cut into the desired dimension using diamond wires. Mild steel specimens were mechanically polished successively with the help of emery papers of grades 100, 200, 300, 400 and 600 micron and then thoroughly cleaned with plenty of triple distilled water and then with acetone. Duplicate in some case triplicate experiment were performed to check the reproducibility of data.

2.17.2. Weight loss by corrosion at room temperature

Corrosive environment of varying concentrations (The various concentrations of chloride, sulphate, sulphite, nitrite, and phenol and cyanide ion solutions) were prepared and kept in a bottle of 300ml capacity. After recording of initial weights, Metal coupons were dipped into the corrosive media using a thread attached to the cork covering the bottle opening. The samples were left in this state unscathed and undisturbed for a period of seven days. It was done to allow proper time for corrosion to take place. After the completion of seven day period metal coupons were taken out and cleaned with jet of water and lightly scrubbed to remove loosely bounded scales. Sample was weighed to measure the direct corrosion loss. Sometimes Increase in weight was reported showing deposition of scales.

In figure 2.1 and figure 2.2 shows the photographic view of the experimental setup used for the room temperature studies. Figure 2.1 represents the photographic view on the first day of batch study (at room temperature 32- 34°).Figure 2.2 represents the setup after seven days of different environment at different concentrations

Figure 2.1: The photographic view of experimental setup of room temperature studies at the intial stage.

Figure 2.2: The photographic view of experimental setup of room temperature studies at the final stage.

2.17.3. Weight loss by corrosion at high temperature

Weight loss experiments were carried out in an electronically controlled heating mental (perfectly insulated)with distillation apparatus set up maintained at a constant temperature of 100°C within an accuracy of ±0.1°C.Two mild steel coupons were exposed to boiling corrosive environment at 100˚C.. A condenser setup was used to ensure that the concentration of the electrolyte remains unchanged. Samples were exposed for half an hour in one single run. Multiple runs were done in a few cases to verify the reproducibility of data. Once the

experiment was complete, samples were immediately removed from the corrosive media to avoid error due to prolonged exposure. Samples were cleaned by jet of water and soft scrubbing to remove any loosely bounded scales. Sample was weighed to determine direct corrosion loss.

Scale and film formed on Surface was cleaned using metal brush and sample was weighed to determine overall corrosion rate and weight of scales.

2.17.4. Corrosion inhibition study

The experimental study was performed at different concentrations at room temperature (32-350C) and at high temperature (100^0C).The immersion time for room temperature experiment was 7 days and for high temperature was 30 minutes. The results of the weight loss experiment were from the mean of two runs; each with a fresh specimen and fresh 200 ml wastewater solution. The corroded nails were weighted before and after the immersion period and then the percentage of the Inhibition Efficiency (IE) was calculated.

2.18. SCALE ANALYSIS

2.18.1. Scanning Electron Microscopy (SEM) Technique and EDX

This scheme was applied to focus on the surface study of mild steel samples to study about the nature and type of corrosion. By the use of SEM method the behaviour of mild steel sample with its surface has been deeply analysed and further followed by the analysis of corrosion type. From the fresh mild steel samples micrographs has been obtained and it is compared with the micrographs of specimen which is already corroded. This particular sample of mild steel which has been used for study is collected from the industry. The dimensions of sample should be between 5-8 mm and should not exceed be 10 mm for the correct and best results. The surface of the specimen is finished by using the polishing meter with 400 mesh sand paper, and cleaned using acetone for the removal of dust. Samples have to be mounted on a circular metallic sample holder. Since an electron beam is incident on the samples for SEM analysis, it is essential that the samples are electrically conducting. If not, this can be achieved by coating the samples. The magnification range was started from 500X to 20000X and the magnified images of cracks or pits were captured. For the analysis of elemental peaks the complementary of SEM, EDX analysis has been done. Inside the beam the electron beam is generated by the X-rays, this phenomenon occurs in EDX. Most of the X-ray carries the energy of element which is emitted by them, hence if we compute the X-ray energy, we can also know which elements are there in the sample. The samples should be

FLAT for accurate quantitative analysis. For qualitative analysis any shape of the sample is workable.

2.11.1.1Sample preparation

Metal Coupon was cleaned with emery paper of multiple grits in the range of 80-300. The coupon obtained was washed and cleaned. The Scanning Electron Microscopy was done using JEOL Scanning Electron Microscope. The resolution and magnification range of SEM was 3.5 nm and '10X to 400,000 X' respectively. Corroded samples for SEM imaging were obtained from Rourkela Steel Plant. Ii was a part of machinery equipment replaced due to corrosion.

2.11.2X-Ray Diffraction (XRD Technique)

X-ray diffraction is a preferable method for the compound analysis. In X-ray diffraction appropriate preparation of powder sample is most essential parameter, to gain signal to noise ratio and to overcome the fluctuations in the intensity, to avoid spottiness and minimize preferred orientation fine graded particles should be used for XRD. Reduction of powders to fine particles also ensures enough particle participation in the diffraction process. The preferable sample size is it should pass through a 325 mesh sieve (45 μm).The specimen sample is fixed in the sample holder with a glass slide; the surface is slightly pressed with soft emery paper. The angle specified for rotation (2ɵ) is chosen as 2 degrees. The obtained plot is analysed using Xper thigh score software for the investigation of the peaks present in the sample.

3. RESULTS AND DISCUSSIONS

In the present study, we determine the properties of material and environments, the two factors playing a major part in corrosion. Features of the environment i.e. pH, turbidity, dissolved oxygen content, biological and chemical oxygen demand, concentration of various chemical components present. The Industrial Wastewater Sample was collected from Coke Quenching pit of SAIL (Steel Authority of India), Rourkela. Preservation techniques were used to preserve the composition of the sample to the time of analysis as per the conservation techniques provided by the environmental protection agency. For metal coupons, weight loss in corrosive environment was used to determine their susceptibility to the environment. Weight loss was measured at two different temperatures such as one low temperature at ambient and other at 100˚C.

3.8. ENVIRONMENT ANALYSIS

Industrial Waste Water sample from Rourkela Steel Plant, which acts as an environment for their quenching, waste water treatment and pumping unit was used to determine the nature of the corrosive environment. On analysing the sample for different components, using various methods suited to them, the composition of the industrial water was found to be the following

Table 3.1: Analysis of waste water from Coke quenching Plant

Component	Amount in ppm	
	Run 1	Run 2
Biological Oxygen Demand	110.56	105.00
Dissolved Oxygen Content	10.00	9.80
Chemical Oxygen Demand	508.80	513.70
Hardness	400.96	412.04
Phenol	70.08	72.81
Sulphate	7.68	18.20
Chloride	223.00	192.00
Nitrite	0.20	0.34
Ammonia	116.80	
Total Kjeldahl Nitrogen	246.60	

3.1.1. Biological Oxygen Demand

The biological oxygen demand of the sample collected from the coke quenching plant was estimated using the appropriate protocol of Environmental Protection Agency. From the

multiple runs of the experiment, the result was obtained to be 110.56 mg/l. The available plant data shows the result obtained is within the range of 63.90 - 92.30.

3.1.2. Dissolved Oxygen Content

The dissolved oxygen content of coke quenching plant sample was found out by Winkler's method, and it was obtained as 10 mg/l. The corrosion rate is directly proportional to the amount of dissolved oxygen present in the testing sample. Based on the available plant data the observed data comes in the range (15 – 40 mg/l)

3.1.3. Chemical Oxygen Demand

Chemical Oxygen Demand of the sample collected from coke quenching plant is found by using the protocol available in the Environmental protection agency manual. The chemical oxygen demand (COD) was determined to be 508.8 mg/l. The COD range reported in the literature is given by 525.39 – 810.30 mg/l the observe data lies in this range.

3.1.4. Hardness

The hardness of the sample collected from the cock quenching plant was found as 400.96 mg/l. Hardness is the property of sample due to the presence of carbonates and bicarbonates, these are responsible for the corrosion of mild steel by increasing the pH of the sample. The observed value is overall getting match with the literature values; it lies in the range of 440.21 - 495.39 mg/l.

3.1.5. Phenol

The amount of phenol present in the sample collected from coke quenching plant is analysed by using the spectrophotometric method. The intensity of the formed dye shows the amount of phenol present in the sample. The amount obtained as 72.01 mg/l. The range of phenol level reported in the literature is given by 81.20 - 123.60, mg/l the observed value is lies this range. Phenol is highly reactive, and they undergo biodegradation. The biodegradation of phenol liberates oxygen and the corrosion activity increases. They break the passive layer formed on the metal surface.

3.1.6. Sulphate

The sulphate content of the sample collected from coke quenching plant was found out by gravimetric method (by precipitation of barium sulphate).The concentration of sulphate ions was determined as 7.68 mg/l. The sulphate levels are very high than that observe in the literature (0.60 – 0.70 mg/l),so the amount of sulphur compounds plays a very significant role in the corrosion.

3.1.7. Chloride

The amount of chloride present in the coke quenching plant sample was examined by Mohr's method (titration).The result was obtained as 223 mg/l. The chloride amount is high enough to cause corrosion towards mild steel and they showed the pitting corrosion pattern. The low-level concentrations of chlorides are favourable because they work as a disinfectant. At high levels they show very severe corrosion effects to mild steel. The Chloride level in the observed literature is given by 480.00– 600.00 mg/l, the decrease in this level shows because they are really reactive and easily get evaporated form the solution.

3.1.8. Nitrite

The spectrophotometric analysis the amount of nitrite content present in the sample collected from the coke quenching plant. The amount present in the sample was determined to be 0.2 mg/l. As per literature very less quantity of nitrite also causes very vigorous corrosion it usually undergoes the pitting corrosion, the normal level of nitrites are reported as 0.10 – 0.40 mg/l.

3.1.9. Ammonia

The ammonia content present in the quenching plant sample was found out by the spectrophotometric method. The ammonia content of the sample was found as 116.8 mg/l. The reported values in the literature are 80 – 140 mg/l. presence of ammonia shows the corrosion due to nitrogen compounds.

3.1.10. Total Kjeldahl Nitrogen

Kjeldahl nitrogen stands for all the organic nitrogen present in the sample. The sample collected from cock quenching plant was analysed by the Kjeldahl distillation process. The TKN value was obtained 246.6 mg/l. The amount of TKN is fairly high enough for the corrosion of mild steel. The amount in the literature is given as 336.93 – 562.30its getting overall match with observed value. Table 3.2 compares the result obtained with the data available in the literatures

Table 3.2: Comparison of obtained results and the literature values (M.K.Ghosh, 2001; R Krishnaveni et al., 2013)

Component	**Amount in mg/l**	
	Observed	**Literature**
Biological Oxygen Demand	110.56	63.90 - 92.30
Dissolved Oxygen Content	10.00	15.00– 40.00
Chemical Oxygen Demand	508.80	525.39 – 810.30
Hardness	400.96	440.21 - 495.39
Phenol	70.08	81.20 - 123.60
Sulphate	7.68	0.60 – 0.70
Chloride	223.00	480.00– 600.00
Nitrite	0.20	0.10 – 0.40
Ammonia	116.80	80.00– 140.00
Total Kjeldahl Nitrogen	246.60	336.93 – 562.30

3.9. SEM and EDX Analysis

Scanning Electron Microscope was used to determine the composition and morphology of the metal samples. Initially the composition of the fresh sample, as well as a corroded sample, was studied to contrast the change brought in the composition of the surface due to corrosion. Figure 3.1 explains the morphological structure of the corroded sample. The Cracks and pits are visible on the surface. At the end of the experiment diameter of the pits were measured, 42.5micrometres. The exact measurements are difficult because of the presence of the corrosion products deposited around the pits.

The corrosion products are of the composition carbon, oxygen and sulphur. These results are obtained from the EDX analysis. The results of elemental analyses of non-corroded and corroded samples are tabulated in Table 3.3. These two are compared to find out the deposited products.

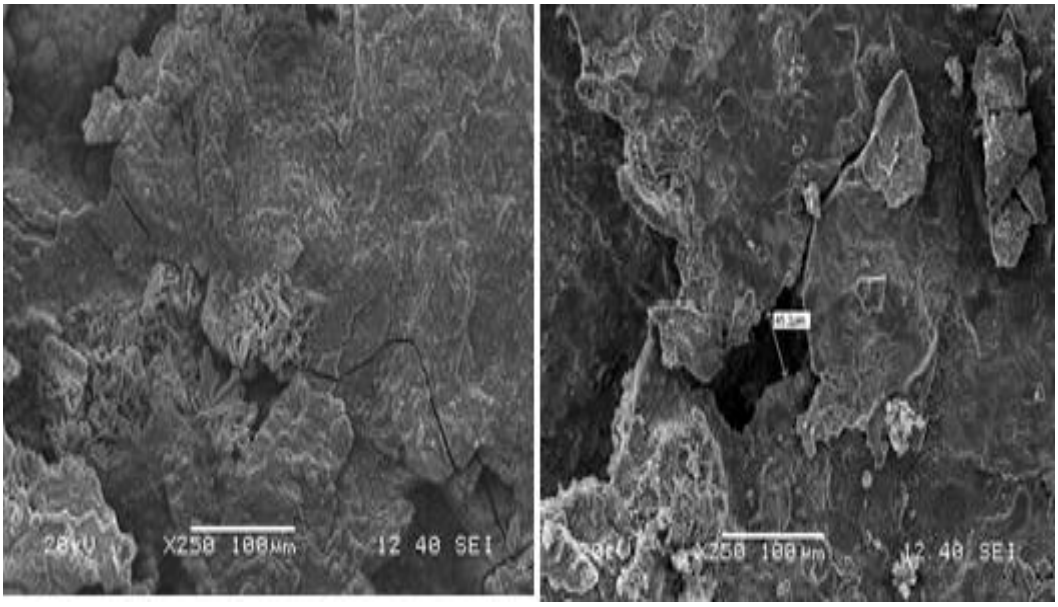

Figure 3.1: Surface deterioration by (a) Cracking and (b) Pitting

Table 3.3: Composition of mild steel samples (Corroded and non-corroded)

Component	Weight (%) Corroded Sample	Weight (%) Free Sample	Component	Weight (%) Corroded Sample	Weight (%) Free Sample
Iron	60.88	95.35	Sulphur	1.44	-
Carbon	6.62	2.53	Cadmium	1.09	0.04
Oxygen	28.77	-	Nickel	-	0.49
Magnesium	0.93	-	Zinc	-	1.24
Aluminum	0.25	-	Titanium	-	0.10
Silicon	0.04	-	Lead	-	0.25

3.10. XRD Analysis

X-ray crystallography is used for identification of the crystal and molecular structure, by measuring the angles and intensities of the refracted beams. The analysis of two different corroded samples was done and the results obtained are as shown in figure 3.2.This technique measures the spacing between the particles layers, thus determines the orientation and the crystal size of the unknown material. The obtained results are compared with the standard JCPDS card number and the unknown compounds present in the sample are found

out. The compounds present in the testing sample were obtained is shown in with their structures in table 3.4.

Table 3.4: Samples and their corresponding crystal structure

Compound Name	Crystal Structure
Fe_2O_3(Hematite)	Hexagonal Crystal Structure
$FeCO_3$(Siderite)	Hexagonal Crystal Structure
Fe_3O_4(Magnetite)	Cubic Crystal Structure
FeO	Cubic Crystal Structure

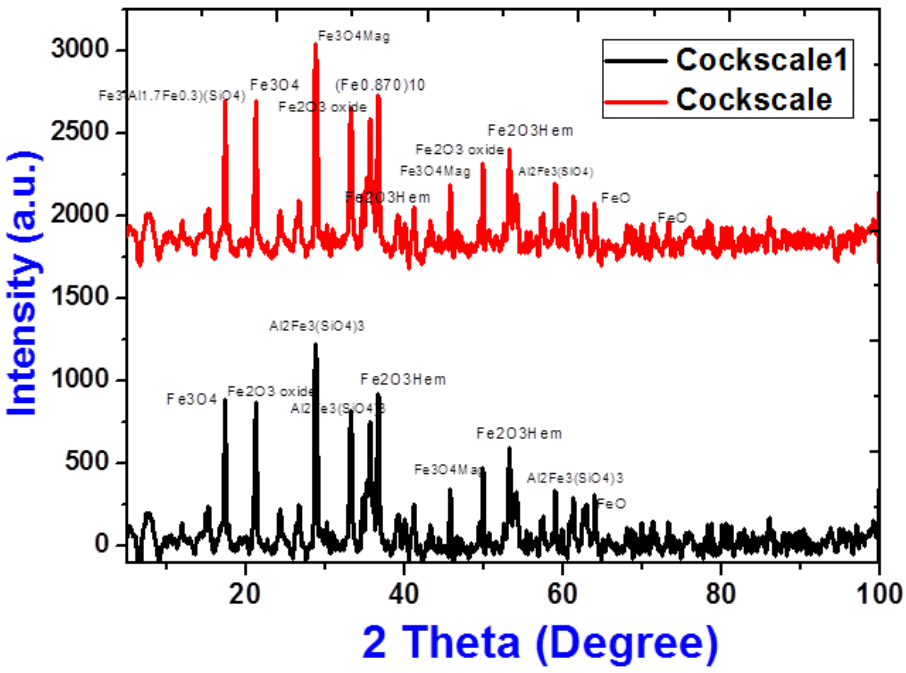

Figure 3.2: XRD Analysis of Corroded samples

3.11. Weight Loss Experiment

3.4.1 Corrosion of Sample at Room Temperature.

The sample was tested with various concentrations of multiple electrolytes to determine the corrosion and the critical concentration at which the corrosion rate is maximum. The Experiment has been done at room temperature (32 – 36 °C).The variation of corrosion rate with the concentration of different irons with an 2 percent error bar is also included for the each effects discussed in the following section..

3.4.1.1 ONE PARAMETER STUDY

3.4.1.1.1 Effect of Chloride

The effect of chloride ions on the corrosion of mild steel is discussed in the chapter 1.Figure 3.3 represents the rate of corrosion with the increase in the concentrations of chloride ions. Corrosion rate has been found to rise initially in the concentration range of 10-50 mg/l but decrease as the concentration is increased. . This reduction in corrosion rate is due to the formation of stable passive film over the surface that prevents the metal from further corrosion. The corrosion rate is almost stagnant in the region of 100-200 mg/l due to this passivity. The sample obtained after the seven days batch experiment was also having firmly attached film to it, it was very hard to remove and at 10 to 50 mg/l concentration range the pits was visible.

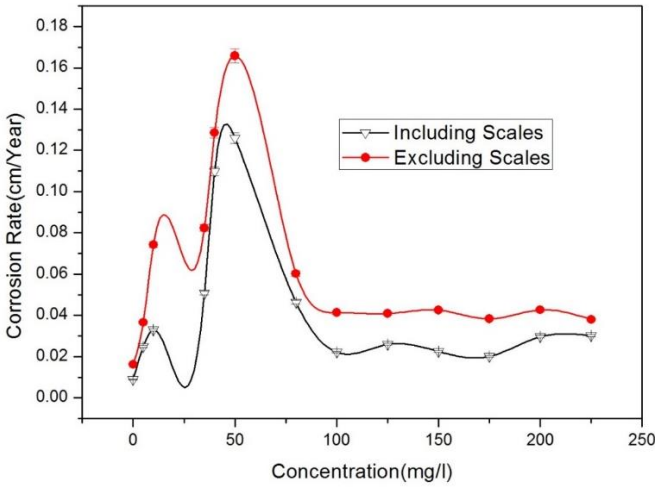

Figure 3.3: Variation in corrosion rate with concentration of chloride ions at room temperature

3.4.1.1.2 Effect of Phenol

The detailed discussion of effects of phenol on the mild steel is reported in the previous chapter 1. Figure 3.4 shows the variation of rate of corrosion with the concentration of phenol. Phenol has been found to have corrosive effect in low concentration range which tends to decrease as concentration is increased. A very interesting phenomenon to observe in case of phenol was simultaneous decrement in scale deposition and direct metal loss (Overall loss – scales formed).

The samples taken from the seven days batch experiment, and the scale formed was fragile and yellowish brown in colour. It was easy to remove, as concentration increases the film

removal was getting hard. As the film thickness decreases, the corrosion rate was getting increases.

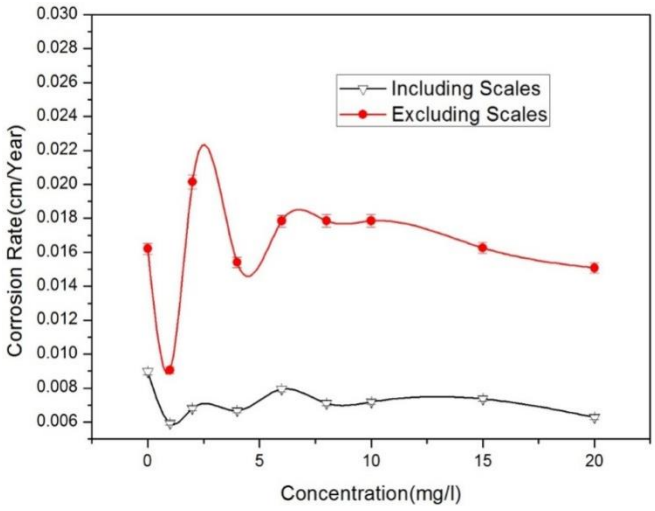

Figure 3.4: Variation in corrosion rate with concentration of Phenol at room temperature

3.4.1.1.4 Effect of Sulphates.

The sulphur compounds are very reactive towards the mild steel, the detailed studies are given in the chapter 1.Figure 3.5 shows the variation of corrosion rate with the concentration of sulphate ions. Direct metal loss rate has been almost consistent over the concentration range of 5-20ppm. Direct metal loss has shown an increasing tendency beyond this concentration. Variation of overall metal loss to direct loss tends to confirm the effect of passivity due to film formation. Whenever the overall metal is increasing, a downward shift can be observed in the direct metal loss. The scales formed on the surface after the batch series experiments were attached to the material surface. Strong and thick scale were developed with an increase in concentration of sulphate ions. Film developed was difficult to remove and difficulty increased with concentration as the scale thickness increased, the corrosion rate got reduced.

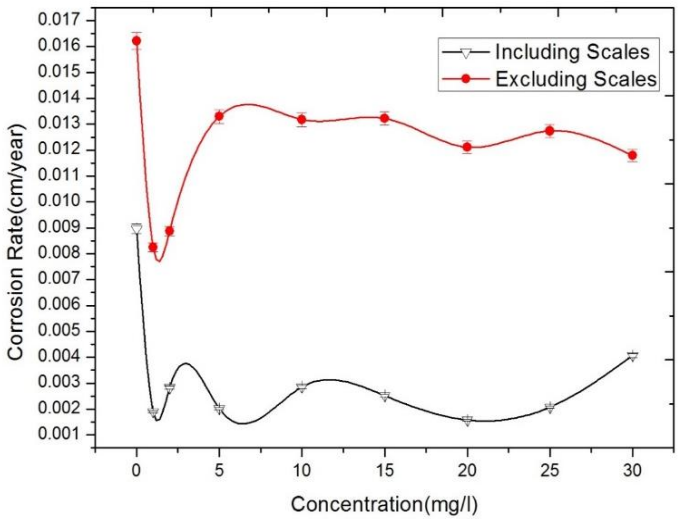

Figure 3.5: Variation in corrosion rate with concentration of Sulphate ions at room temperature

3.4.1.1.5 Effect of Nitrites

The detailed effect of nitrites on the mild steel corrosion is discussed in the chapter 1.Figure 3.6 represents the variation in rate of corrosion with the increase in the concentration of nitrite ions. With an increase in concentration of nitrites, both direct and overall metal loss has shown a downward trend. This trend shows an active passive film formation by nitrites over the metal surface.

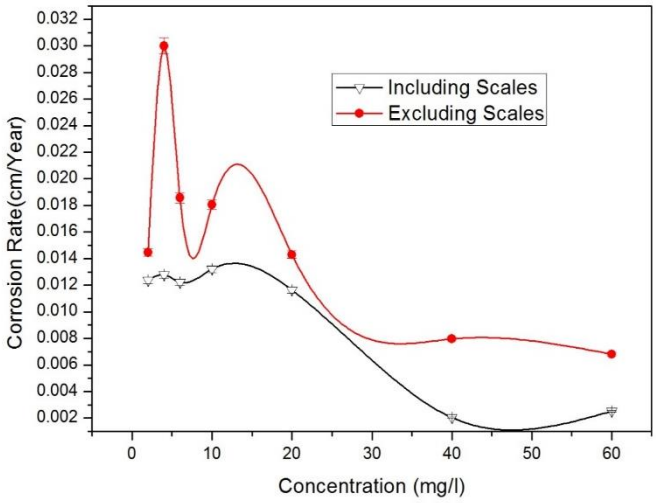

Figure 3.5: Variation in corrosion rate with concentration of Nitrite ions at room temperature

Differences between the two losses are comparatively small further confirming the strength of film against corrosion. As the scale thickness and the corrosion rate are inversely proportional to each other at the lower concentrations. After reaching a certain maximum corrosion rate point, it started decreases and got constant. At higher levels, the scale thickness and the corrosion rate became independent of concentration.

3.4.1.1.6 Effect of Sulphites

The detailed study of sulphites towards the corrosion of mild steel is discussed in the chapter 1.Figure 3.7 shows the variation of corrosion rate with the variation of sulphite ions. Sulphites ions have shown accelerated corrosion in compared to the ions discussed before. Both the type of losses tends to run parallel keeping the rate of scale formation constant with increasing concentration. With an increase in concentration, corrosion rates are increasing.

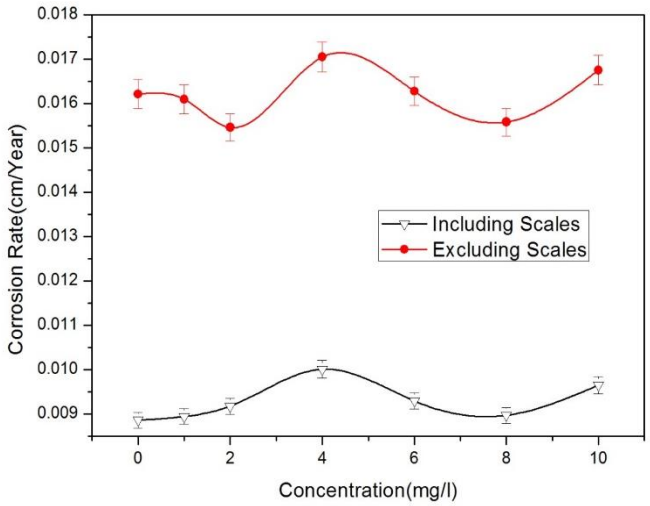

Figure 3.6: Variation in corrosion rate with concentration of Sulphite ions at room temperature

3.4.1.1.7 Effect of Ferricyanides.

The effect of cyanides on the corrosion of mild steel is discussed in the previous chapter(chapter 1).Figure 3.8 represents the variation of rate of corrosion with the increase in the concentration of ferricyanide ions. Ferricyanides appear to be highly corrosive in nature. Corrosion rates have a positive trend with an increase in concentration. Scale deposition decreases in the concentration range of 20-30 ppm only to gain the momentum later. The sample after seven days batch test the scales formed was firmly attached to the surface of the testing sample, the colour of the thin film was greening black colour. The scales were very hard to remove, on the surface pits was visible.

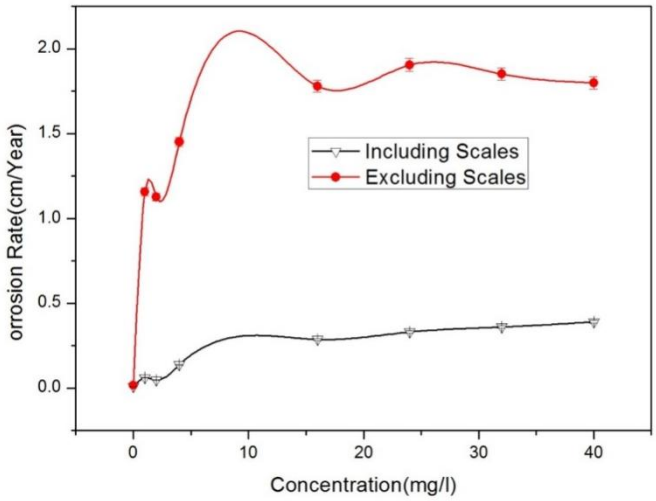

Figure 3.7: Variation in corrosion rate with concentration of ferricyanide ions at room temperature

3.4.2 Effect of High temperature using Boil tests.

The sample was boiled for half an hour and weight loss was measured to understand the impact of concentration along with temperature.

3.4.2.1 ONE PARAMETER STUDY

3.4.2.1.1 Effect of Chloride

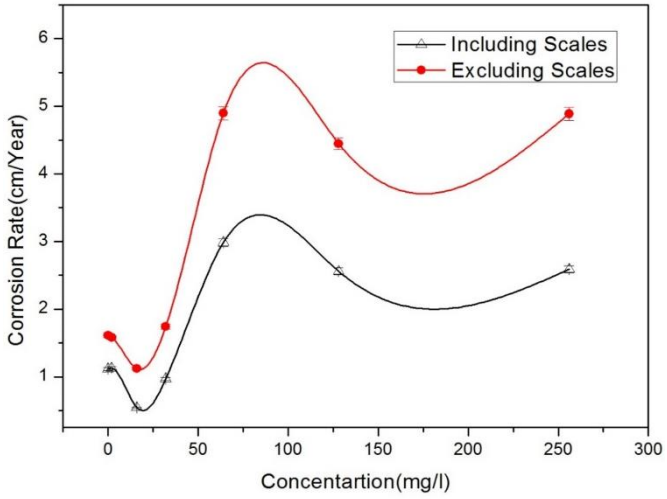

Figure 3.8: Variation in corrosion rate with concentration of chloride ions at 100˚C

Figure 3.9 represents the variation of rate of corrosion with increase in the concentration of chloride ions at 100°C. Very high corrosion rates are observed with an incremental tendency with concentration. As concentration is increased, corrosion rates are increasing. At lower concentrations the temperature rate is directly proportional to the corrosion rate, a sharp decrease in the corrosion occurs at about 25 ppm then it getting increases, by reaching about 150 ppm again decrease in corrosion rate and increases again, this behaviour shows that the

formed layer is not tightly attached to the surface and the layer formed is not stable enough to withstand the attack of chloride ions.

3.4.2.1.2 Effect of Phenol

Figure 3.10shows the variation of corrosion rate with increase in the concentration of phenol at 100°C. Phenols have their maximum effect in the range of 40-70 ppm at high temperature. This trend decreases in 70 -80 ppm, with a positive slope as concentration further increases. As the concentration increases over 100 mg/l there a slight rise in the corrosion rate it shows that the passive film started the deterioration

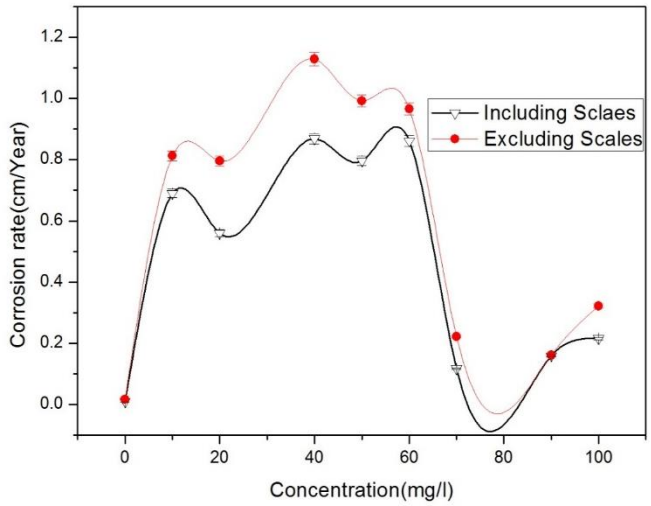

Figure 3.9: Variation in corrosion rate with concentration of Phenol at 100˚C

3.4.2.1.3 Effect of Sulphates

Figure 3.11 shows the variation of rate of corrosion with increase in the concentration of sulphate ions at 100°C.

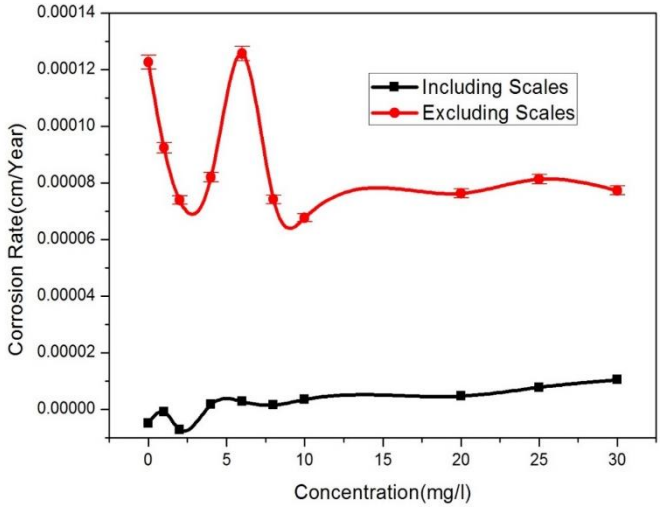

Figure 3.10: Variation in corrosion rate with concentration of Sulphate ions at 100˚C

Direct Metal loss is maximum at 15 ppm while overall metal loss is maximum at a lower concentration of 5ppm. The increase in direct loss is a result of weak film formation that allows the metal surface for prolonged contact with an electrolyte. As concentration increases, direct corrosion tends to rise while overall metal loss decreases due to lack of film formation.

3.4.2.1.4 Effect of Nitrites

Figure 3.12 represents the variation of corrosion rate with the increase in the concentration of nitrite ions at 100°C.Nitrite ions are very corrosive in nature. In the concentration range of 10-15 ppm, they are showing heavy corrosion that seizes as concentration is increased. With an increase in concentration, rapid film formation is taking place that inhibits the corrosive effect. After the high-temperature treatment of 30 minutes, the samples taken from the distillation unit will be having a thin layer formed on the surface. At lower concentrations the developed layer will be loosely bounded as the concentration getting increases the layer will be firmly attached to the surface, thus the corrosion going sharply reduces.

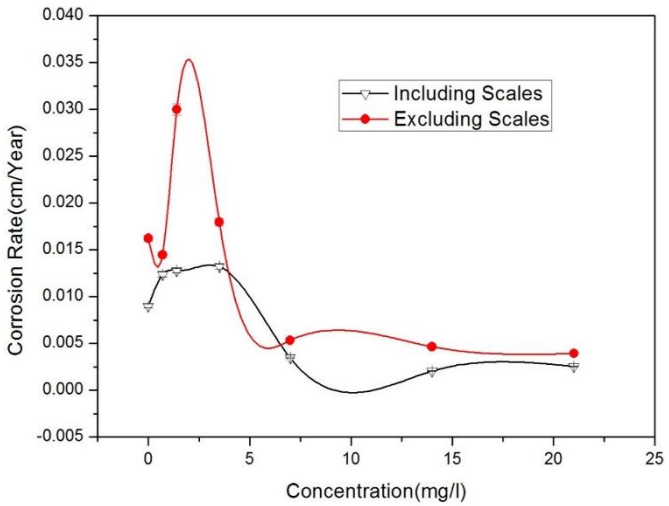

Figure 3.11: Variation in corrosion rate with concentration of nitrite ions at 100˚C

3.4.2.1.5 Effect of sulphites

Figure 3.13 Shows the variation of corrosion rate with increase in the concentration of sulphite ions at 100°C.Sulphite ions are shown film formation that is inefficient to prohibit the effect of corrosion. With the increase in concentration, overall metal loss is increasing but the direct metal loss remains almost constant.

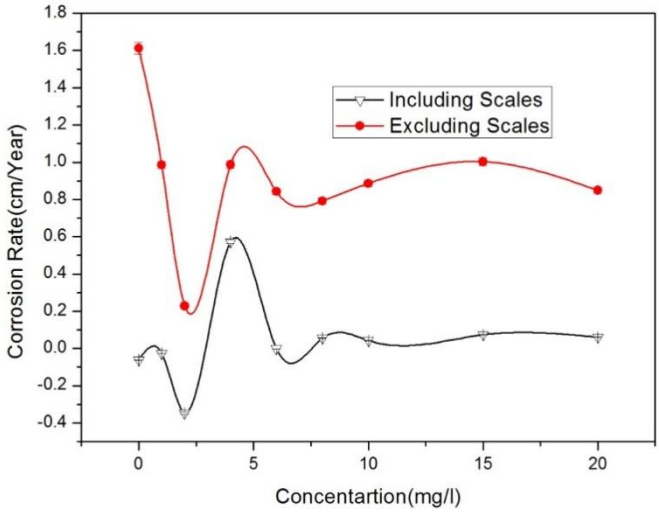

Figure 3.12 Variation in corrosion rate with varying concentration of Sulphite ions at 100˚C

The increment in scale formation doesn't have any adverse effect on direct corrosion; this suggests the permeable nature of film formed. The samples after high-temperature treatment will show a thin film on the surface but it is very loosely bounded and they may show passive nature towards the sulphite ions; thus the corrosion rate increases sharply.

3.4.2.1.6 Effect of Ferricyanides

Figure 3.14 represents the variation of rate of corrosion with the increase in the concentration of ferricyanide ions at 100°C. With an increase in concentration, direct metal loss is increasing almost linearly. In low concentration range, overall corrosion is high depicting large-scale formation, although, in the concentration range of 20-40, overall corrosion is decreasing and direct corrosion is increasing. It shows the gradual decrement in film formation as concentration increases.

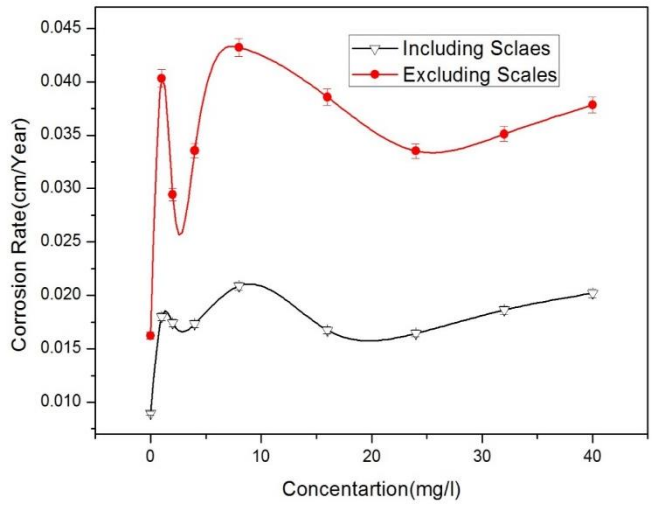

Figure 3.13: Variation in corrosion rate with concentration of ferricyanide ions at 100˚C

The steel specimen after high-temperature treatment, a thin passive layer is formed on the surface but the thickness of the layer is independent of the corrosion rate. After a peak in the corrosion rate, the corrosion rate is getting constant.

3.4.2Corrosion of Samples at room temperature

3.4.2.1 TWO PARAMETER STUDY

3.4.2.1.1 Effect of 1:1 Chloride and Nitrite combination

Figure 3.15 shows the variation of corrosion rate with the increase in the concentration of the 1:1 combination of chloride and sulphate ions. At the lower concentrations as the passive layer thickness increases the overall corrosion rate is also an increase. At a particular point both of the corrosion reaches a constant value and continues at steady state. This shows a strong effect of the formed passive layer. The formed passive layer will be strongly attached to the surface and this determines the corrosion rate.

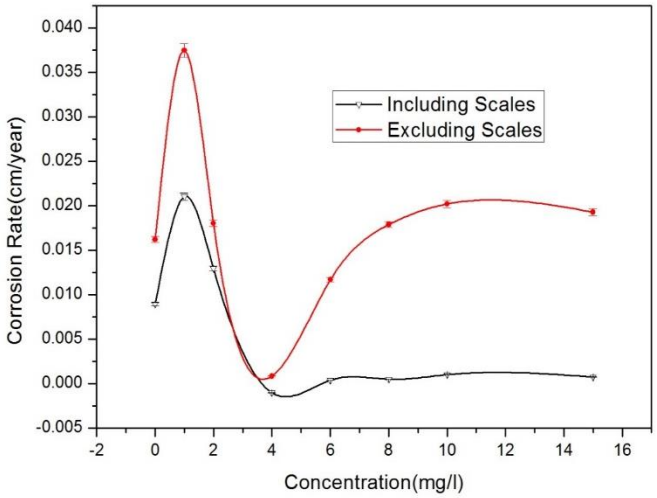

Figure 3.14: Variation in corrosion rate with concentration of 1:1 combination of chloride and Nitrite ions at room temperature

3.4.2.1.2 Effect of 1:1 Sulphate and Nitrite combination

Figure 3.16 shows variation of corrosion rate with increase in the concentration of the combination of 1:1 sulphate and nitrite combination. At lower concentrations as the passive layer thickness increases the corrosion rate is also increases. As the concentration getting increased the passive layer thickness increases the overall corrosion rate getting constant. This shows the effect of passive layer on the corrosion, the passive layer is strongly attached to the surface thus the ions are not penetrating to the surface because of that the corrosion rate is getting constant.

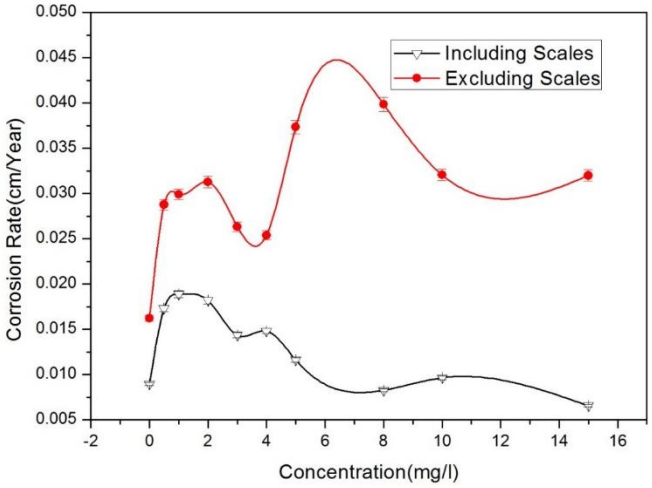

Figure 3.15: Variation in corrosion rate with concentration of 1:1 combination of Sulphate and Nitrite ions at room temperature

3.4.3Effect of High temperature using Boil tests

3.4.3.1 TWO PARAMETER STUDY

3.4.3.1.1 Effect of 1:1 Chloride and Nitrite combination

Figure 3.17 shows the variation of corrosion rate with the increase in the concentration of the combined solution (1:1 proportions).This clearly denotes the change in direct corrosion with the weight of scales formed. As overall corrosion increases, direct corrosion tends to decrease due to passive film formation. Further, an interesting result is the reduced rate of corrosion when compared individually with nitrite or chloride. This shows inhibition effect one on another. The high temperature treated mild steel specimen is showing a direct relationship between the thin passive layer formed and the corrosion rate. As the passive layer thickness is large the corrosion rate is low, the passive layer thickness decreases the corrosion rate increases and vice versa.

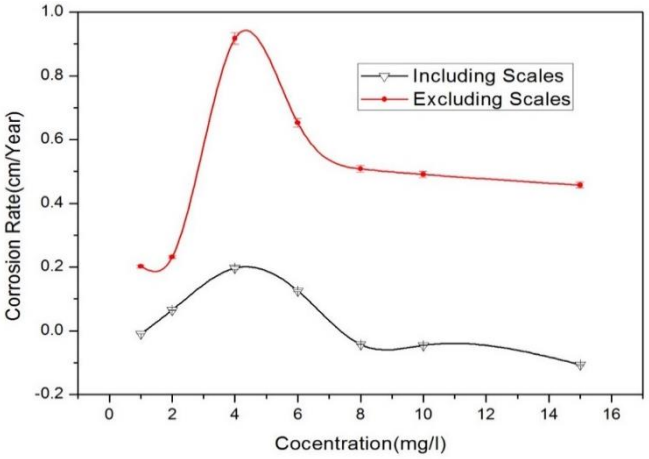

Figure 3.16: Variation in corrosion rate with concentration of 1:1 combination of chloride and Nitrite ions at 100˚C

3.4.3.1.2 Effect of 1:1 Sulphate and Nitrite Combination

Figure 3.18 shows the variation of corrosion rate with the concentration change of the combination of sulphate and nitrites. The combination is less corrosive than the individual electrolytes. A passive film formation is taking place. Passivity is increasing with increment in the thickness of scales over the surface. Direct corrosion is increasing with increasing concentration. Maximum corrosion is taking place at 10ppm. At this point, the amount of film deposition is minimum. In this combination method also we can conclude that the corrosion rate is directly proportional to the passive layer thickness formed. For high corrosion rate, the thickness of the layer formed will be very loosely packed and thin.

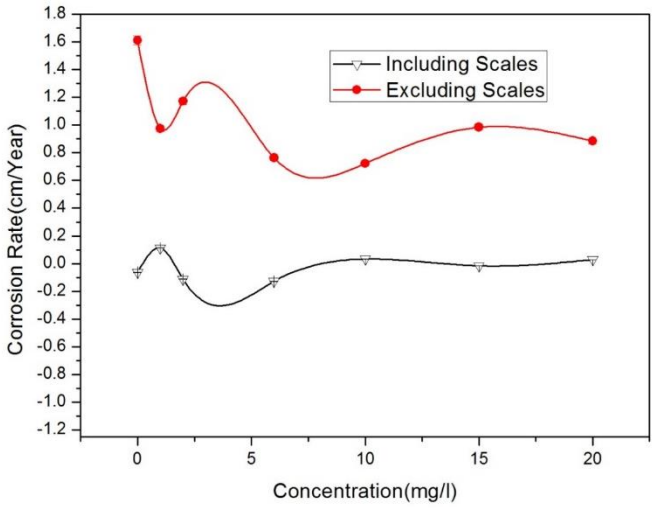

Figure 3.17: Variation in corrosion rate with concentration of 1:1 combination of Sulphate and Nitrite ions at 100˚C

3.4.3 Corrosion of Samples at room temperature

3.4.3.1 THREE PARAMETER STUDY

3.4.3.1.1 Effect of 1:1:1 combination of Sulphate, Nitrite and Chloride.

Corrosion rate are less compared to all the three individually. Although as the concentration increases, direct metal loss is decreasing with increment in overall loss. Here also we can get a direct relationship between the thickness of the scales formed and the corrosion rate. As the thickness getting increases the rate of corrosion is getting reduces. At the initial stages (lower concentrations) the thickness of passive layer has no effect on the corrosion. As the concentration increases they show a directly proportional.

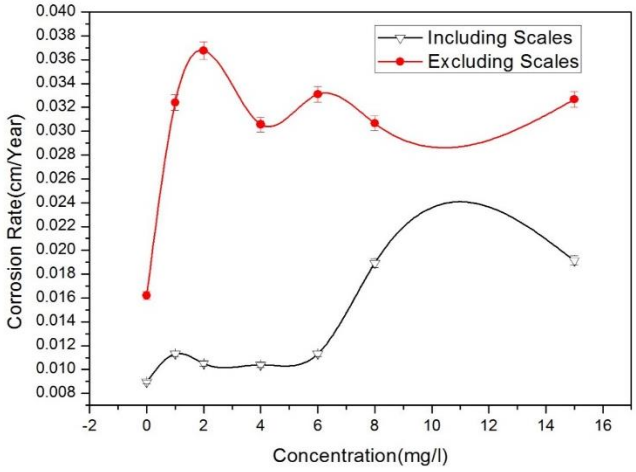

Figure 3.18: Variation in corrosion rate with concentration of 1:1:1 combination of Sulphate, Nitrite and Chloride Ions at room temperature

3.4.3.1.2Effect of 1:1:1 combination of Sulphate, Nitrite and Chloride.

Figure 3.20 shows the variation of corrosion rate with the change in the concentration of the 1:1:1 combination mixture at room temperature. Corrosion rate are less compared to all the three individually. Although as the concentration increases, direct metal loss is decreasing with increment in overall loss. It can be attributed to the formation of thick passive film at higher concentrations. Increase in concentration increases weight of scale formed. In this experiment also we can directly correlate the thin passive layer formed and the corrosion rate of the mild steel sample. At high concentrations the passive layer formed have no effect on the corrosion rate.

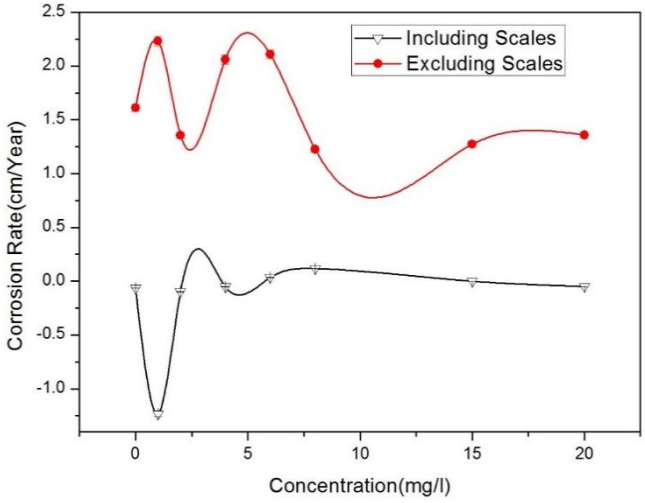

Figure 3.19: Variation in corrosion rate with concentration of 1:1:1 combination of Sulphate, Nitrite and Chloride Ions at 100°C

3.5 Effect of Aniline as Corrosion Inhibitor.

Table 3.5 Maximum corrosive concentrations

Electrolyte	Most Corrosive conc. at room temperature.(ppm)	Most corrosive conc. At 100˚C.(ppm)
Chloride	50	250
Phenol	2	40
Sulphate	5	6
Nitrite	10	2
Sulphite	10	15
Cyanide	40	40

In this part of the experiment, metal sample is again allowed to react with electrolytes. This time electrolytes have the concentration at which maximum rate of corrosion was recorded in previous experiments. The maximum corrosive concentrations are enlisted in the table 3.4.

3.5.1 Corrosion Effect by Electrolyte with aniline at Room Temperature

Figure 3.21 shows the variation of corrosion rate with different components with the addition of aniline.

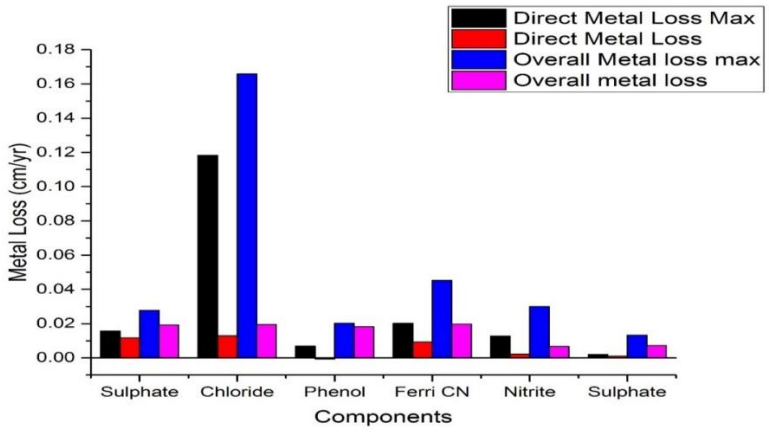

Figure 3.20: Variation of corrosion rates in presence of Aniline as an additive (1 ppm) to the solution

It is evident from the experiment that, in presence of Aniline there is a considerable decrease in corrosion rate. Amount of scale formed has reduced as well as the corrosion. Aniline leads to a thin and strong film formation over the metal which inhibits further corrosion. Aniline

has shown maximum inhibition efficiency in case of chlorides while minimum in case of phenol.

Table 3.6: Corrosion Inhibition efficiency of Aniline at Room Temperature

Component	Inhibition Efficiency % in Direct Loss.	Inhibition Efficiency % in overall loss.
Sulphite	24.44	30.70
Chloride	89.10	88.21
Phenol	110.53	7.43
Ferricyanide	54.05	56.31
Nitrite	83.22	77.85
Sulphate	50.35	45.54

3.5.2 Corrosion Effect by Electrolyte with aniline at High temperature

Figure 3.22 shows the variation of corrosion rate with different components without the addition of aniline. It is observed Aniline loses its knack as an inhibitor at high temperatures. Interesting observation is that in case of Phenol and Sulphate at boiling temperature, it enhances their corrosive tendency.

Table 3.7: Inhibition efficiency corresponds to the maximum corroded mixtures. at high temperatures

Corrosive Environment	Inhibition Efficiency% in Direct Loss	Inhibition Efficiency% in Overall Metal Loss
Sulphate	49.03	17.91
Chloride	80.93	81.48
Phenol	251.93	-52.31
Ferricyanide	47.44	4.50
Nitrite	-360.11	83.66
Sulphate	-209.10	-47.06

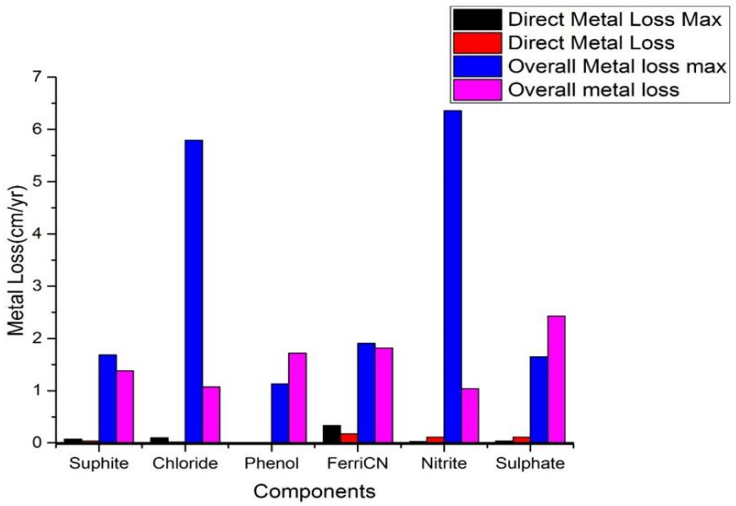

Figure 3.21: Effect of Aniline at maximum concentration in contrast with "Absence of Aniline

3.5.3. Comparison of corrosion by industrial water with and without aniline.

In this part of the experiment, metal sample is again allowed to react with the sample collected from industry with and without the addition of aniline. The overall corrosion rate was found to decrease by the use of aniline.

Table 3.8: Corrosion rates for Quenching Pit Wastewater

Solution	Corrosion Rate for Direct Loss in cm/yr.	Corrosion rate for overall Loss in cm/yr.
Wastewater from Quenching Pit	0.00362	0.010356
Wastewater from Quenching Pit with Aniline added	0.002516	0.009782

4. CONCLUSION AND FUTURE SCOPE

4.1 CONCLUSION

In the present study the investigation of corrosion effects under the industrial simulated conditions were studied. The type of corrosion present in the surface was determined by the surface morphological techniques like SEM, EDX and XRD analysis. The quantification of different compounds responsible for corrosion of equipment due to water used for the purpose of quenching process. The material loss due to individual and combined effects under simulated industrial conditions at specified temperatures. The salient features of the findings were outlined below.

- Surface observation by SEM analysis gives us the information regarding the type of corrosion. From the corrosion sample micrographs, we can infer that the formed corrosion is of pitting and cracking type (these are visible on the surface). From the component analysis its shows the presence of oxygen, sulphur and carbon, and it has been found that the surface corrosion or imperfection is mainly caused by the attack of these elements.
- Based on the XRD analysis, significant amount of FeO, Fe_2O_3 and Fe_3O_4 were present, which forms a layer on the surface that plays a significant role in the corrosion. Mainly based on the thickness of these layers they can inhibit the corrosion attack considerably, but the cracks on these layers will leads to the corrosion.
- The wastewater sample reacting with the mild-steel were analysed and the result obtained was matching overall with the literature of the coking plants facing corrosion problems. The BOD, COD, DO and hardness was found to be 110.56, 508.80, 10 and 400.96 mg/l respectively. These parameters indicate the presence of considerable amount of oxygen, which is directly proportional to the rate of corrosion. So the increased values of these parameters show an increased corrosion rate.
- The concentration of phenol reduces with time due to biodegradation and this decreases the pH of the solution which leads to severe corrosion. The sulphate content (7.68mg/l) of the water sample is much higher as compared to the values reported in the literature. Even at lower concentrations, presence of sulphate ions results in severe corrosion formation on surface.
- The two other parameters that account for corrosion are the amount of nitrogen compounds (includes ammonia, nitrites and organic nitrogen) and chlorine. The nitrite at lower concentration itself forms pits. The chlorine content in the investigated sample was

found to be 223 mg/l. Even though it is a very high amount, the size of the chloride ion is small, so they can easily penetrate to the surface and a rigorous localized corrosion occurs.

- From the weight loss method, the individual effects of the components and the role of formed passive layer on the corrosion inhibition was studied. For most of the elements like nitrites, sulphates chlorides etc. shown a significant effect on the passive layer formed on the surface at room temperature. As the temperature increases the passive layer started braking and corrosion rate was increased.
- Aniline is a good corrosion inhibitor nature as per the literature study. It is most efficient against corrosion due to chlorides and least against phenols as per the resulted values: 81.48 % and -52.31 %. At high temperature, aniline loses its inhibiting effect and is responsible for corrosion in presence of phenols and sulphates.

4.2 FUTURE SCOPE

- Inhibition capacity should be investigated with more compounds.
- How these inhibitors can be used at Industrial level to stop large scale corrosions.

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APPENDIX I

(Calibration curves)